IOP Conf. Series: Materials Science and Engineering **739** (2020) 012019 doi:10.1088/1757-899X/739/1/012019

Encapsulate Materials Effect on $Zn_xCd_{1-x}S$ White Light Quantum Dots-Based White Light-Emitting Diodes

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Abstract. In this study, colloidal ternary $Zn_xCd_{1-x}S$ white light quantum dots (WQDs) were prepared, which have the characteristics of broad emission window. We used epoxy, styrene ethylene butylene styrene block copolymer (SEBS), and silicone as encapsulate materials to pack the device. The results show that the $Zn_{0.5}$ and $Zn_{0.8}$ have band edge and surface state emission. The quantum yield (QY) and particle size of $Zn_{0.5}$ and $Zn_{0.8}$ WQDs is 19, 32 % and 4.5$\pm$0.5 and 3.1$\pm$0.5 nm, respectively. The white light-emitting diodes (WLEDs) were obtained by mixing WQDs with different resins, and pumping by UV chip. The luminous efficacy is 6.7 and 8.5 lm/W for $Zn_{0.5}$ and $Zn_{0.8}$-based WLED by using epoxy resin as encapsulate material. Moreover, the long period test can maintain 201 and 184 h for $Zn_{0.5}$ and $Zn_{0.8}$-based WLED, respectively. The results of this study present that the device encapsulated by epoxy resin can improve the luminous efficacy and stability of device. This outstanding finding may contribute to the future development of solid-state lighting (SSL).

1. Introduction

Quantum dots (QDs) have high quantum yield (QY), wavelength tunability and broad excitation band [1], so they can be applied to many applications, such as solid state lighting (SSL) [2, 3] and display [4]. In order to improve the disadvantage of color rendering and self-absorption effects of commercially available white light emitting diodes (WLEDs) [5, 6], the white light quantum dots (WQDs)-based WLEDs were developed. The WQDs can cover the entire visible light range because of its broad emission window, and preparation of high color rendering WLEDs [7]. However, the low luminous efficacy and low stability of device limits the application in solid state lighting (SSL). The luminous efficacy and stability of WLEDs are affected by the transparency of the encapsulate materials. The compatibility between encapsulates and QDs is influence the performance of WLED. Chung et al. reported that the Zn0.5 and Zn0.8 WQDs were used silicone resin to pack WLED, the luminous efficacy of Zn0.5 and Zn0.8 are 1.0 and 4.1 lm/W [8], while used polyurethane Acrylic (PUA) UV resin to pack WLED, the luminous efficacy of Zn0.8 increases to 11.9 lm/W, and the long period test can maintain for 10 h [9]. In this study, three types of encapsulate materias are selected to form WLEDs, and the performances of WLEDs are compared.

2. Experimental

2.1. Chemicals

Cadmium oxide (CdO, 99.99 %) was purchased from Alfa Aesar. Stearic acid (SA, 99 %), zinc oxide (ZnO, 99.99 %), Sulfur (S, 99.99 %), 1-octadecene (ODE, 90 %), hexadecylamine (HDA, 90 %), and trioctylphosphine oxide (TOPO, 90 %) were purchased from Sigma-Aldrich. Epoxy was purchased from Everwide Chemical Co., Ltd., SEBS block copolymer was purchased from Phon Tech Industrial Company, and silicone and UV chip provided by Lextar Electronics Corporation. The standard dye, rhodamine 101, used in quantum yield (QY) measurement, was also purchased from Aldrich. Hexane (99.7 %) and methanol (99 %) gotten from Macron Chemicals. All chemicals were used as received without purification.

2.2. Synthesis of $Zn_xCd_{1-x}S$ quantum dots

0.15 mmol of CdO and 0.15 mmol of ZnO for $Zn_{0.5}$, 0.06 mmol of CdO and 0.24 mmol of ZnO for $Zn_{0.8}$ and SA were placed in the three-necked flask and then heated to 230 ^{o}C under Ar flow. CdO, ZnO and SA powder was dissolved until the solution transfer to optical transparent with light yellow color. Meanwhile, the solution was cooled down to room temperature. HDA and TOPO were added into above solution and stirred together under Ar at room temperature, and then reheated up to 320 ^{o}C. S powder dissolved in ODE injected rapidly into the reaction flask and reacted at 290 ^{o}C to growth $Zn_{0.5}$ and $Zn_{0.8}$ QDs. After reacted for 60 min, the solution was cooled down to room temperature to stop the reaction. Samples were purified by adding methanol, and then dispersed in hexane for further measurement.

2.3. Preparation of white light-emitting diode

The $Zn_{0.5}$ and $Zn_{0.8}$ QDs blended with epoxy, SEBS, and silicone gel under different weight ratios, and then putted above mixture into 413 nm UV chip and cured at room temperature. The performance of WLEDs such as CIE coordinates, correlated color temperature (CCT, K), color rendering index (CRI) and luminous efficacy measured by integrating sphere. The samples were named as $Zn_{0.5}$-$LED_{y,z}$ and $Zn_{0.8}$-$LED_{y,z}$. The y means the type of gel, and z means the weight percentage of QDs.

*2.4. Characterization *

The optical properties of samples measured with UV-vis spectrometer (UV-vis, Hitachi UH-5300 spectrometer) and fluorescence spectrophotometer (FL, Hitachi F-7000). Relative QY of samples was determined by comparing the peak area under the curve of FL emission for the $Zn_{0.5}$ and $Zn_{0.8}$ QDs with that of fluorescent dye (rhodamine 101 in ethanol). Transmission electron microscope (TEM, JEOL JEM-2010) was used to analyze the morphologies and size distribution of samples. The LED measuring system (ISUZU Optics, SLM-6Z) is used to measure the performance of devices.

3. Results and Discussion

3.1. FL spectra and TEM images of $Zn_xCd_{1-x}S$ QD

The absorption and emission spectra of $Zn_{0.5}$ and $Zn_{0.8}$ QD shows in figure 1. We can find that the $Zn_{0.5}$ and Zn0.8 QD have very broad emission window, which combines with band edge and surface state emission [8]. The band edge emission peak and QY of Zn0.5 and Zn0.8 QDs are 429, 409 nm, and 19, 32 %, respectively. Moreover, band edge emission is blue shift with increasing Zn content due to the larger band gap of ZnS. The photographs of Zn0.5 and Zn0.8 QD stored in the hexane under UV light is also shown in figure 1. The light color is warm and cold white light for Zn0.5 and Zn0.8 QD, respectively. This result is consistent with that reported by Siao and Chen et al. [8-11] In the TEM images we can find that the morphology of Zn0.5 and Zn0.8 is spherical with 4.5±0.5 and 3.1±0.5 nm

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and the size distribution is uniform.

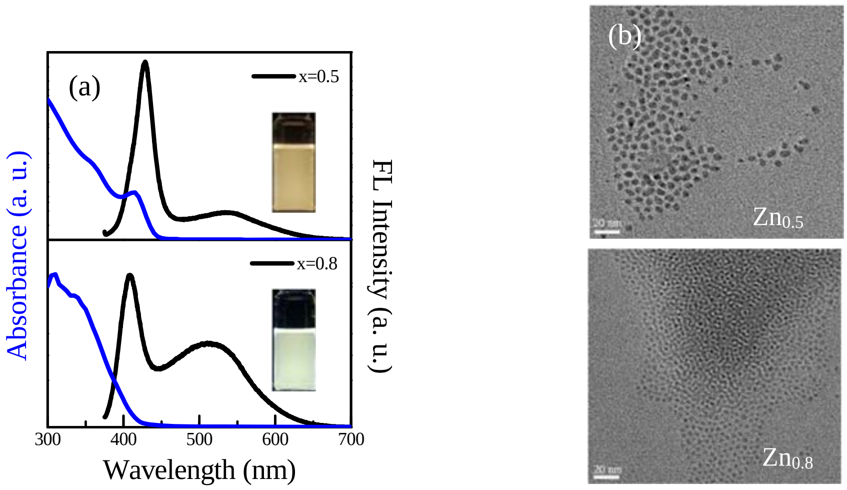

Figure 1. (a) Absorption and emission spectra and (b) TEM image of samples. Insert photograph in (a) shows the $Zn_{0.5}$ and $Zn_{0.8}$ QDs under UV irradiation.

3.2. White light-emitting diodes

The $Zn_{0.5}$ and $Zn_{0.8}$ used as light conversion materials to form WLED. The EL spectra and CIE coordinates of WLED show in figure 2, and the light transmittance of encapsulates show in figure 3. We can find that the EL intensity of Zn_x-LED_{epoxy} is higher than that of Zn_x-LED_{SEBS} and Zn_x-$LED_{silicone}$ significantly, and the CIE coordinates close to the position of warm white light. We can find that the transmittance of epoxy and silicone film is higher than 80 % in visible light range, while that of SEBS is lower 80 %. The luminous efficacy of $Zn_{0.5}$-$LED_{epoxy,50}$, $Zn_{0.5}$-$LED_{SEBS,80}$ and $Zn_{0.5}$-$LED_{silicone,67}$ are 6.7, 5.2 and 5.9 lm/W, and that of for $Zn_{0.8}$-$LED_{epoxy,33}$, $Zn_{0.8}$-$LED_{SEBS,50}$ and $Zn_{0.8}$-$LED_{silicone,33}$ are 8.5, 5.6 and 8.0 lm/W, respectively. The results are summarized in table 1. The stability of Zn_x-$LED_{y,z}$ is shown in figure 4. The long period test of $Zn_{0.5}$-$LED_{epoxy,50}$, $Zn_{0.5}$-$LED_{SEBS,80}$ and $Zn_{0.5}$-$LED_{silicone,67}$ can maintain 201, 28 and 4 h, and the reliability for $Zn_{0.8}$-$LED_{epoxy,33}$, $Zn_{0.8}$-$LED_{SEBS,50}$ and $Zn_{0.8}$-$LED_{silicone,33}$ are 184, 161 and 44 h. We can find that the luminous efficacy and reliability of Zn_x-LED_{epoxy} is better than that of Zn_x-LED_{SEBS} and Zn_x-$LED_{silicone}$, owing to the light transmittance of the epoxy is the highest, and the compatibility with QDs is the best.

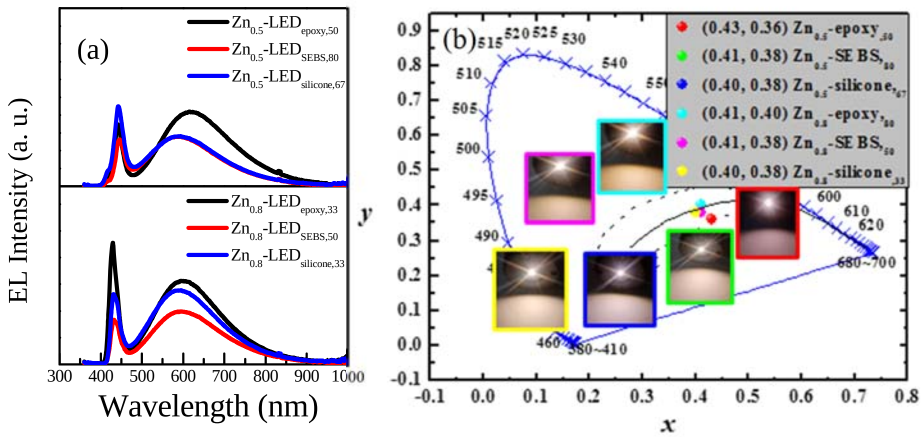

Figure 2. The EL spectra (a) and CIE coordinates (b) of Zn_x-$LED_{y,z}$. Insert photographs show the devices under 20 mA injection current.

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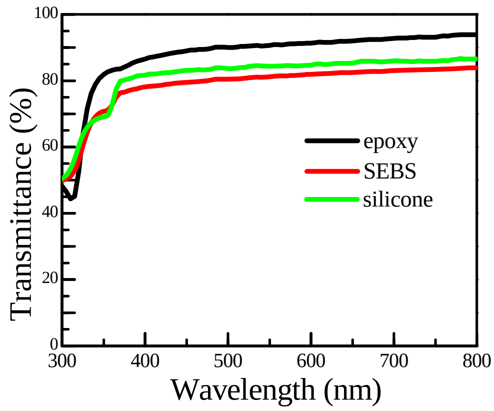

Figure 3. The transmittance of epoxy, SEBS, and silicone.

Table 1. The properties of Zn_x-$LED_{y,z}$.

QD	gel	CIE (x, y)	CCT (K)	CRI	Efficacy (lm/W)
$Zn_{0.5}$	$epoxy_{50}$	(0.43, 0.36)	2760	85	6.7
	$SEBS_{80}$	(0.41, 0.38)	3776	86	5.2
	$silicone_{67}$	(0.40, 0.38)	4508	90	5.9
$Zn_{0.8}$	$epoxy_{33}$	(0.40, 0.35)	3379	83	8.5
	$SEBS_{50}$	(0.41, 0.38)	3392	83	5.6
	$silicone_{33}$	(0.40, 0.38)	3593	83	8.0

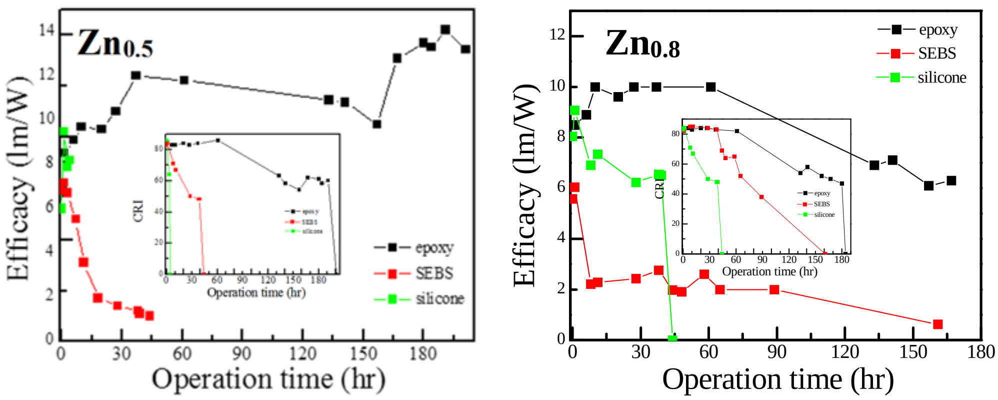

Figure 4. Stability of Zn_x-$LED_{y,z}$ for long period of working time under 20 mA. Insert diagram shows the CRI variation of devices.

4. Conclusion

In conclusion, we present a facile thermal pyrolysis organometallic route to synthesize white light Zn_x WQDs, and used epoxy, SEBS and silicone mixed WQDs to pack WLED. We can find that $Zn_{0.5}$ and $Zn_{0.8}$ QD have broad emission window, and QY is 19 and 32 %, respectively. The morphology of $Zn_{0.5}$ and $Zn_{0.8}$ QD is spherical. Using epoxy as encapsulate material, the $Zn_{0.8}$-$LED_{epoxy,33}$ device have the best luminous efficacy of 8.5 lm/W and operating time for 184 h. This study shows that the high light transmittance of the encapsulate material and the good compatibility of the QDs enhance the luminescent properties of the WLED.

Acknowledgement
This work was supported by the Ministry of Science and Technology of Taiwan under Contract nos. 107-2221-E-150-034 and 108-2221-E-150-016.

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