Investigation of stability and optical performance of quantum-dot-based LEDs with methyl-terminated-PDMS-based liquid-type packaging structure

JIASHENG LI,1,2 YONG TANG,1 ZONGTAO LI,1,2,* XINRUI DING,1 LONGSHI RAO,1 AND BINHAI YU1

1Engineering Research Center of Green Manufacturing for Energy-Saving and New-Energy Technology, South China University of Technology, Guangdong 510640, China
2Foshan NationStar Optoelectronics Company Ltd., Foshan 528000, China
*Corresponding author: meztli@scut.edu.cn

Received 22 October 2018; accepted 18 November 2018; posted 21 November 2018 (Doc. ID 348859); published 20 December 2018

Although quantum dots (QDs) have a high quantum yield close to one in a solution, they exhibit low conversion efficiency in a solidification polymer matrix, which hampers the development of QD-based light-emitting diodes (LEDs) with high stability and optical performance. In this study, we proposed a methyl-terminated-polydimethylsiloxane (PDMS)-based liquid-type packaging structure (LPS) to improve stability and optical performance of QD-based LEDs. Compared with the traditional ethylene-terminated-PDMS-based solid-type packaging structure, the LPS with an optimized kinematic viscosity of 10000 m²/s can provide higher stability and optical performances for QD-based LEDs, including total radiant power and luminous flux. Consequently, the proposed effective and simple strategy has great potential for illumination and display applications.

© 2018 Optical Society of America

https://doi.org/10.1364/OL.44.000090

Quantum dots (QDs) have become one of the most promising color-conversion materials in light-emitting diodes (LEDs) owing to their high quantum yield (QY) and simple fabrication [1]. They have great potential for replacement of the conventional rare-earth-based phosphor (REP) materials [2]. Although their QY has improved over 90% [1], CdSe/ZnS QDs [3] still cannot achieve a radiant efficacy (luminous efficacy) comparable with that of REP when used in LEDs [4]. In addition to the aggregation and reabsorption issues, when QDs are concentrated in large quantities [5,6], another significant challenge is that the QDs can be destroyed during the matrix exchange processes [7,8]. In general, QDs were synthesized in solutions including water, organic solvent, and paraffin, which is challenging to use directly in LED packaging [9]. Therefore, QDs need to be redispersed in a silicone-based encapsulant and then packaged with LEDs [10]. During the matrix exchange and curing processes, the polymer chain can interact with QDs through chemical force and can even be replaced with their ligands [11], which may destroy QD structure. Therefore, the QY of QDs in a solidification polymer matrix is still significantly lower than that in a solution [8]. In order to overcome the low efficiency of QDs in the solid state, Kuo et al. [12] have sealed a QD solution in a glass box and then assembled it on LEDs, achieving a significantly high luminous efficacy owing to the presence of QDs in the liquid state. However, the solution used for QDs is toxic and volatile, and requires more complex packaging processes. Consequently, it is desired to develop other environment-friendly and stable liquid matrices for QDs packaged in LEDs.

Polydimethylsiloxane (PDMS) is a highly transparent material with high thermal and optical stabilities [13] and great potential for applications in liquid-type packaging of QD-based LEDs. In this study, we proposed a methyl-terminated-PDMS (mt-PDMS)-based liquid-type packaging structure (LPS) to improve the stability and optical performance of QD-based LEDs. The kinematic viscosity of the mt-PDMS was optimized to improve stability and prevent QD sedimentation. Finally, the optical performances, including radiant power, luminous flux, and spectra of QD-based LEDs with LPS, were compared with those of QD-based LEDs with the conventional ethylene-terminated-PDMS-(et-PDMS)-based solid-type packaging structure (SPS).

Oil-soluble green CdSe/ZnS QDs with a core/shell structure were purchased from China Beijing Beida Jubang Science and Technology Co., Ltd. (QY: 90%, emission peak: 520 nm). The mt-PDMS with a kinematic viscosity in the range of 50 m²/s to 10000 m²/s, and et-PDMS including a curing agent with a kinematic viscosity of 3500 m²/s were purchased from Dow Corning; both of them were transparent, almost without absorption of visible light. A chloroform solution was purchased from Aladdin Reagents. Blue-LED devices were purchased from Foshan NationStar Optoelectronics Co. Ltd. (emission wavelength centered at 455 nm), shown in Fig. 1(b). QD/PDMS composites were fabricated based on the evaporation

Vol. 44, No. 1 / 1 January 2019 / Optics Letters
Letter
0146-9592/19/010090-04 Journal © 2019 Optical Society of America
method [14]. First, QDs were added into 1.5 mL of the chloroform solution. The mass of QDs was adjusted to determine their concentration in the PDMS matrix; 2.0 g of PDMS were then added into the QD solution and stirred for 50 min in a planetary-type stirring machine with evacuation. This process was aimed to uniformly disperse QDs in the PDMS matrix by evaporating the chloroform solution. After this step, the QD/PDMS composites were directly filled in the blue-LED devices through an injection hole, as shown in Fig. 1(a). Finally, these devices were placed in an oven and cured at a temperature of 125°C for 30 min. Although the mt-PDMS could not undergo the cross-linked reaction, the LEDs with the LPS should also be heated at the same conditions as those of the LEDs with SPS to avoid the influence of thermal aging in the comparison. The injection current for all of the LEDs was 200 mA (electrical injection power of 0.66 W), provided by a Keithley source. The fabricated LEDs with LPS, without and with injection current, are shown in Figs. 1(c) and 1(d), respectively.

One of the advantages of et-PDMS is that the fixed silicone network can prevent QD sedimentation in LEDs. However, the polymer chain of mt-PDMS is flexible, which allows a certain QD movement, leading to sedimentation. Therefore, we optimized the kinematic viscosity of mt-PDMS according to an aging test (environmental temperature of 25°C, without injection current). The LEDs with the LPS and SPS had the same QD concentration of 0.6 wt. % in the aging test. Figures 2(a)–2(e) show the total radiant power, radiant power of the chip light (light emission from an LED chip with wavelength from 400 nm to 500 nm), radiant power of the QD light (light emission from the QDs with wavelength from 500 nm to 600 nm), luminous flux, and QD light proportion (ratio of the QD light radiant power to the total light radiant power) of the QD-based LEDs, respectively. Figure 2(a) shows that a smaller kinematic viscosity of mt-PDMS is beneficial to increase the total radiant power with the increase of aging time. Figures 2(b) and 2(c) show that this increment is due mainly to the enhancement in radiant power of the chip light. A reasonable explanation is that QDs can more easily settle in mt-PDMS with a lower kinematic viscosity during aging processes. These settled QDs at the bottom of the LEDs were challenging to excite by the chip light; the QD concentration above the LED chip decreased, leading to less color-conversion events. Consequently, significantly more chip light can directly escape from the LEDs without undergoing absorption by the QDs, decreasing conversion loss. As shown in Fig. 3, the spectra of the LEDs with mt-PDMS (50 m²/s and 10000 m²/s) were used to verify these explanations. When the mt-PDMS with a kinematic viscosity of 50 m²/s was used, a blue shift in the spectral range of 500 nm to 600 nm (QD emission wavelength) was observed with the increase of aging time. This indicates a reduction of the number of reabsorption events with the increase of aging time, owing to the lower QD concentration above the LED chip attributed to sedimentation processes [4]; the higher luminous flux and radiant power of QD light when using 50 m²/s viscosity, as shown in Figs. 2(c) and 2(d), respectively, can also support this explanation. Although the intensity in the spectral range of 500 nm to 600 nm also decreases with the increase of aging time for the LEDs with mt-PDMS with a kinematic viscosity of 10000 m²/s, almost
no shift was observed. This implies that the concentration of QDs above the LED chip does not change after aging. Therefore, the QD sedimentation can be neglected in mt-PDMS when its kinematic viscosity is sufficiently high (10000 m²/s). In addition, it is worth noting that significantly more aggregated QD particles at the bottom of the QD/mt-PDMS (10000 m²/s) composites can be observed after the stirring processes (inset of Fig. 3), as a high kinematic viscosity is not beneficial to fully disperse QDs [7]. The significantly larger number of aggregated QD particles settled at the bottom can lead to a lower QD concentration in the LEDs; therefore, the LED with mt-PDMS with a kinematic viscosity of 10000 m²/s has a higher spectral intensity of the chip light wavelength.

As shown in Figs. 2(d) and 2(e), QD sedimentation can simultaneously lead to lower luminous flux and QD light proportion. When the mt-PDMS with a low kinematic viscosity of 50 m²/s was used, the luminous flux and QD light proportion decreased by 30% and 55% after aging for 100 h, respectively, reducing the light stability of the QD-based LED. It is worth noting that the reduction in luminous flux and QD light proportion when the mt-PDMS with a high kinematic viscosity of 10000 m²/s was used can be even smaller than that for the case of using the et-PDMS after aging. After aging for 100 h, the luminous flux and QD light proportion for the sample with mt-PDMS with a kinematic viscosity of 10000 m²/s decreased only by 10% and 3%, respectively, while for the LEDs with et-PDMS, they decreased by 15% and 10%, respectively. In general, the oxidation in the QDs induced by environmental moisture is the main factor responsible for degradation of QD-based LEDs. The higher stability of LEDs with LPS indicates that the mt-PDMS can provide a better environment to prevent moisture oxidation of the QDs. This can be explained as follows. At the curing processes of et-PDMS, et-PDMS with a C=C bond is linked to the curing agent with a Si–H bond through a hydrosilylation reaction. Simultaneously, the oleic acid ligands with C=C bonds on the surfaces of QDs can also link to the cross-linked network of et-PDMS through hydrosilylation reactions [7,15], as shown in Fig. 4(c). Moreover, the QDs have a large amount of oleic acid ligands on their surfaces. These ligands are competitive to interact with different cross-linked networks of et-PDMS, as shown in Fig. 4(d). As the bonding force of C–Si between the ligand and network is stronger than that of Zn–O between the ligand and QD, these ligands have a higher probability to be removed from QDs under the stretching by different et-PDMS networks with a relatively high rigidity, as shown in Fig. 4(e).

Consequently, a large amount of ligands can be removed from QDs after the curing process of et-PDMS, generating significantly more defects on the surfaces of the QDs, as shown in Fig. 4(b). However, the ligands on the QDs do not interact with mt-PDMS; there is no force to stretch them, providing a more flexible environment, as illustrated in Fig. 4(a). The moisture can reach the CdSe core through the surface defects of the QDs [13], which well explains the result that LEDs with SPS exhibit lower stability than that of LEDs with LPS. As shown in Fig. 2(f), the fewer surface defects of QDs in LPS can be further supported by the higher QY compared with QDs in SPS, leading to a higher luminous flux maintenance in a harsh condition [13] by suppressing thermal quenching [16].

The fewer surface defects of QDs is also beneficial to decrease non-radiant combinations [3], which may increase the light efficiency of LEDs. To further support the above explanation, the initial optical performances (before aging) of QD-based LEDs using the 10000 m²/s mt-PDMS and et-PDMS were compared at different QD concentrations, as shown in Fig. 5. Figure 5(a) shows their total radiant powers and luminous fluxes; both of them for LPS are significantly higher than those for the SPS at different QD concentrations. A larger increment can be observed at higher concentrations; the total radiant power and luminous flux are increased by 52.6% and 41.4%, respectively, at a QD concentration of 0.8 wt. %.

The larger amount of QDs in et-PDMS implies that significantly more ligands are removed from their surfaces, generating a larger loss from non-radiant combinations. Figure 5(b) shows their radiant powers of the chip and QD lights. The LEDs with LPS exhibit higher radiant power of the chip light, indicating that the QDs in mt-PDMS have lower absorption ability with respect to the chip light. As mentioned above, this can be explained as mt-PDMS has a kinematic viscosity higher than that of et-PDMS, causing a significantly larger sedimentation at the bottom of the QD/mt-PDMS composites after stirring. However, the LEDs with LPS exhibit higher radiant power of QD light, though their QDs absorb less chip light. This demonstrates that the QDs have higher conversion efficiency in mt-PDMS, generating significantly more QD light. The QD light proportion determines the output color mixing by QD and chip lights; it is common to compare the optical performances among different LEDs at the same QD light proportion, as shown in Fig. 5(c). The LEDs with LPS also exhibit higher total radiant power and luminous flux, particularly at a higher QD light proportion; compared at the similar QD light proportion of 80% (the correlated color temperature values for LEDs with LPS and SPS are 7266 K and 7349 K, respectively), the total radiant power and luminous flux obtained using mt-PDMS can increase by 23.2% and 26.1%, respectively. These enhancements indicate that LEDs using LPS have great potential in illumination and display applications.

The emission spectra of LEDs with LPS and SPS are shown in Figs. 6(a) and 6(b), respectively. Red shift and expansion can be observed in the spectra with the increase of QD concentration, caused by the reabsorption and aggregation of QDs [17]. Their FWHM values and peak wavelengths are summarized in Fig. 6(c), which are approximately equal at different QD light proportions. This further supports the result that the large improvement in the optical performance obtained by LPS is attributed to reduction in the number of surface defects instead of reductions in reabsorption and aggregation.
In summary, we investigated the stabilities and optical performances of QD-based LEDs with LPS. Compared with traditional SPS, the proposed LPS using mt-PDMS with an optimized kinematic viscosity of 10000 m²/s was beneficial to obtain better stabilities and optical performances of QD-based LEDs. The reductions in luminous flux and QD light proportion caused by LPS were only 10% and 3% after aging for 100 h, while for SPS, they were 15% and 10%, respectively. Moreover, the initial total radiant power and luminous flux for the samples with LPS were increased by 23.2% and 26.1%, respectively, compared with those obtained by SPS at the same QD light proportion of 80%. These results indicate that mt-PDMS can provide a more flexible environment to disperse QDs, preventing ligands' removal from the QDs' surfaces and decreasing the number of surface defects, which is helpful to reduce oxidation and non-radiant combinations. Consequently, the proposed mt-PDMS-based LPS can be an effective and simple structure to improve the performances of QD-based LEDs, with great potential in illumination and display applications.

**Funding.** National Natural Science Foundation of China (NSFC) (51735004, 51775199); Natural Science Foundation of Guangdong Province (2014A030312017); Science and Technology Program of the Guangdong Province (2017B010115001).

**REFERENCES**


