Experimental Investigation on the Moisture Stability of QDs-LEDs With Layered Packaging Structure

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***Abstract*— Quantum dots (QDs)/phosphor hybrid white light emitting diodes (QDs-LEDs) have attracted extensive attention in recent years due to their advantages of high light efficiency and high color rendering index (CRI). However, the QDs present poor thermal and moisture stability, which hinders the commercialization of QDs-LEDs. The layered packaging structure with QDs/silicone film upon the phosphors/silicone film was proposed to improve the thermal stability of QDs-LEDs, while the moisture stability of this packaging structure has not been verified so far. In this study, the moisture stability of QDs-LEDs with layered packaging structure in a high moisture environment with relative humidity of ∼99.8% was experimentally investigated. The results show that the normalized light peak intensity degradations of QDs/silicone and phosphor/silicone films are 12.5% and 54.0% after aging for 178h, which indicates that the moisture stability of QDs is the key factor for determining the moisture stability of QDs-LEDs. The red light peak intensity degradations of QDs-LEDs with QDs/silicone film upon and below the phosphor/silicone film are 21.1% and 8.0% after aging for 178h, indicating that layered packaging structure with QDs/silicone film at the down layer can enhance the moisture stability of QDs-LEDs.**

***Index Terms*— Light emitting diodes, quantum dots, moisture stability, packaging structure.**

I. Introduction

WHITE light-emitting diodes (LEDs) are becoming the most popular lighting source in 21st century, due to their advantages of energy-saving, environmental protection, and high efficiency [1]–[3]. Traditional white LEDs emit light by activating yellow phosphors on a blue light chip and mixing them to produce white light [4]–[6]. But single-phosphor LED suffers poor color rendering index (CRI) when used for lighting. To improve the CRI of white LEDs, some researchers add red fluorescent materials such as red phosphor and Quantum dots (QDs) into the yellow phosphors [7], [8].

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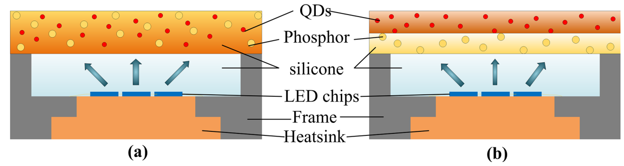

Fig. 1. QDs-LEDs with (a) traditional packaging structure and (b) layered packaging structure.

Compared with phosphor, QDs have the advantages of the narrow spectrum, wide adjustment range, and high quantum efficiency [9], [10], so QDs/phosphors hybrid white LEDs (QDs-LEDs) have attracted extensive attention in recent years. However, there are two drawbacks to the reliability of QDs-LEDs. One is the thermal quenching of QDs occurs at high temperatures [11]–[13], which would significantly reduce the working lifetime of LEDs. Two methods were used to solve the thermal quenching of QDs, one is to develop high thermal conductivity QDs/polymer materials [7], [14], and another is to optimize the packaging structure [7]. Another drawback is the surface ions and ligands of QDs will be eroded by aqueous vapor, resulting in defect trap states [12], [15], [16]. To suppress this defect, two methods were used, one is to coat the nanocrystals with extra ligands [7], and another is to create a barrier layer on the outer surface of polymer film [7], [17].

In the traditional packaging structure, the QDs and phosphors were mixed uniformly in silicone shown as Fig. 1(a). It suffers serious reabsorption between QDs and phosphors, which causes significantly light efficiency drop and increases the working temperature of QDs and phosphors greatly [18], [19]. To solve this problem, some researchers proposed layered packaging structure that separates phosphors and QDs [20], [21] shown as Fig. 1(b). The results show that the working temperature of the QDs and phosphors can be significantly reduced by placing the QDs/polymer film on the top layer [22]. However, some researchers found that phosphors are very stable in high moisture environment, while QDs are very sensitive to the moisture [17]. From this point of view, the reported layered packaging structures with QDs/polymer film at top layer might suffer serious moisture stability problem, especially in high moisture environment. Therefore, more works need to be done to investigate the moisture stability of the QDs-LEDs with layered packaging structure.

In this study, the moisture stability of QDs-LEDs with layered packaging structure in a high moisture environment with relative humidity of ∼99.8% was experimentally investigated.

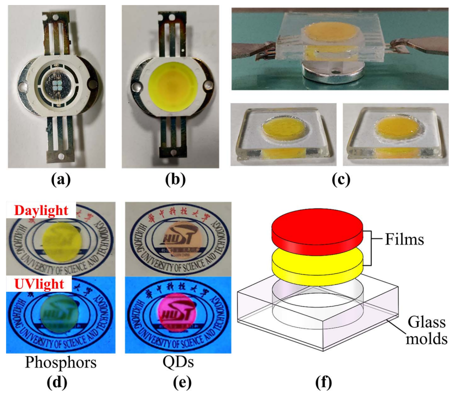

Fig. 2. Pictures of the (a) structure of LED module, (b) white QDs-LED, (c) QDs-LED with remote layered packaging structure, (d) phosphors/silicone film under daylight and UV light, (e)QDs/silicone film under daylight and UV light and (f) Structure of the layered film.

Firstly, the moisture stability of silicone film, QDs/silicone and phosphors/silicone films was investigated. Secondly, the effect of the position of QDs/silicone film (upon or below the phosphor/silicone film) on the moisture stability of QDs-LEDs with layered packaging structure was studied. The normalized red and yellow light peak intensity of QDs and phosphors were measured and analyzed.

II. Experiments

Fig. 2(a) shows the structure of the LED module used in this study. It consists of LED chips, substrate, gold line and a ring dam with diameter of ~12 mm and depth of ~2 mm. The red-emissive CdSe/ZnS core/shell QDs (635nm) and yellow phosphors (550 nm, YAG-O4, Intematix) are mixed with silicone (OE6550, Dow corning) to form QDs/silicone and phosphors/silicone mixtures. The QDs/silicone and phosphor/silicone mixture are coated within the dam to form white QDs-LEDs shown as Fig. 2(b). Except for QDs and phosphors, failure of other packaging components also happens in the moisture environment, such as chip aging, substrate corrosion and gold line fracture. To investigate the moisture stability of QDs and phosphors separately, it is necessary to separate the QDs and phosphors from other packaging components. Therefore, a remote layered packaging structure shown as Fig. 2(c) was proposed. In this packaging structure, the QDs/silicone and phosphors/silicone films with thickness of ~1mm shown as Fig. 2(d) and (e) were fabricated and placed in a glass container in layered structure shown as Fig. 2(f). In the experiments, only the layered films were placed in the moisture environment. The layered films are surround by the glass container and only the top surface contacts with the moisture environment, which is similar to the practical packaging structure of QDs-LEDs.

An experimental setup shown as Fig. 3(a) was built to investigate the moisture stability of QDs-LEDs. It consists of water tank with size of 150 mm × 120 mm × 65 mm, attemperator, temperature and humidity probes. The water tank was heated by the attemperator with temperature of 70 °C. The water evaporates to form a high moisture environment with relative humidity of ~99.8% and temperature of 50 °C. In the experiments, only samples of silicone, QDs/silicone,

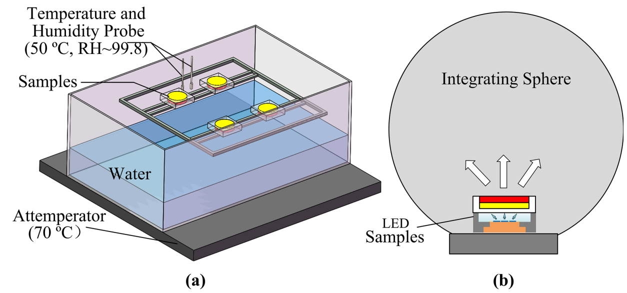

Fig. 3. Experimental setup for measuring the (a) moisture stability and (b) optical performance of the samples.

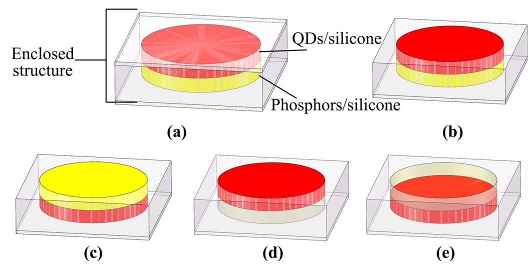

Fig. 4. Experimental samples. (a) Layered film in enclosed glass container, (b), (c) layered films with QDs/silicone upon and below phosphor/silicone film and (d), (e) layered films with QDs/silicone upon and below silicone film.

phosphor/silicone and layered films were placed in the water tank, and the temperature of the films were measured as 50 °C. The films were taken out at regular intervals and placed on the LED module to measure the optical performance of the QDs and phosphors at driving current of 1000 mA by an integrating sphere (ATA-1000, Everfine) shown as Fig. 3(b), and total aging time was set as 178 hours.

Several samples were fabricated and tested in the high moisture environment. 1) Pure silicone, QDs/silicone and phosphors/silicone films were used to characterize the moisture stability of silicone, QDs and phosphors. 2) Layered film with both QDs/silicone and phosphors/silicone films embed in an enclosed glass container shown as Fig. 4(a) was used to characterize the thermal stability of QDs and phosphors in the experimental setup shown as Fig. 3(a). 3) Layered films with QDs/silicone upon and blew the phosphor/silicone film shown as Fig. 4(b) and (c) were used to characterize the moisture stability of QDs-LEDs with layered packaging structure. 4) Layered films with QDs/silicone film upon and blew the silicone film shown as Fig. 4(d) and (e) were used to eliminate the effect of yellow phosphor on the light absorption-conversion process of QDs. The concentration of the QDs/silicone and phosphor/silicone films are 0.5 mg/g and 0.1 g/g. The layered films were fabricated by combining QDs/silicone and phosphor/silicone films by adhesive (OE6550, Dow corning).

III. Results and Discussion

Figure 5 shows the time evolution of normalized light peak intensity of bare LED chips, silicone film, phosphors/silicone film and QDs/silicone film. In the experiments, the LED chips were not exposed to the moisture while the films were completely exposed to the moisture. For the bare LED chips,

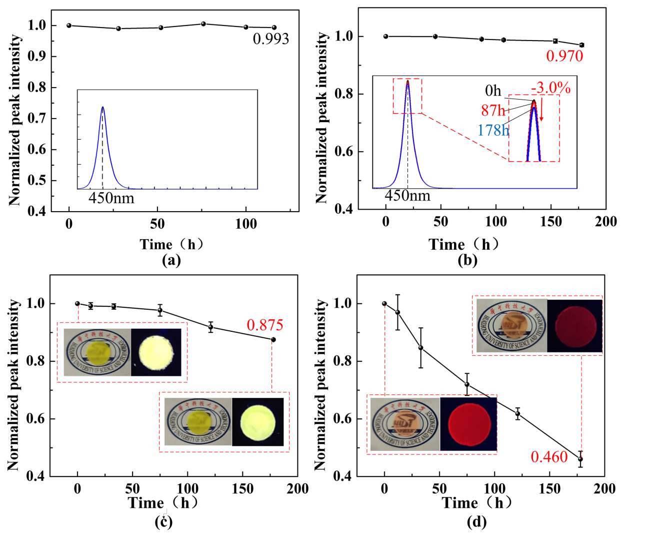

Fig. 5. Time evolution of the normalized light peak intensity of (a) bare LED chips, (b) silicone film, (c) phosphors/silicone film and (d) QDs/silicone film.

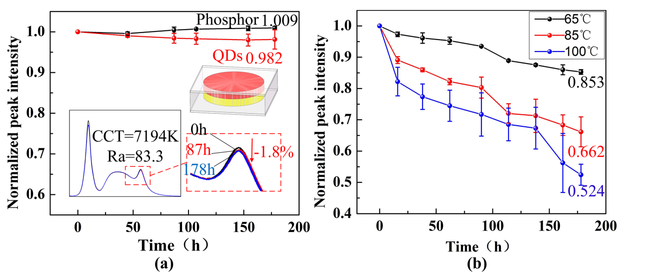

Fig. 6. Thermal stability characterization. (a) Time evolution of normalized yellow and red light peak intensity of the new packaging structure at temperature of 50 °C and (b) time evolution of normalized red light peak intensity of QDs/silicone films at temperature of 65 °C, 85 °C and 100 °C.

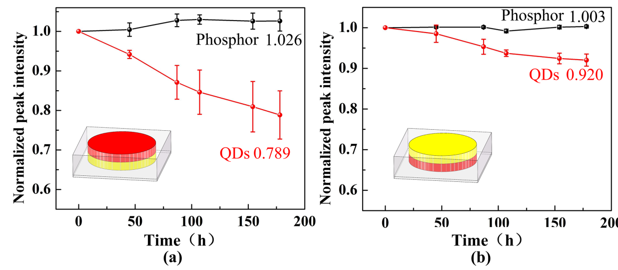

Fig. 7. Time evolution of normalized yellow and red light peak intensity of layered films with QDs/silicone film (a) upon and (b) below the phosphors/silicone film.

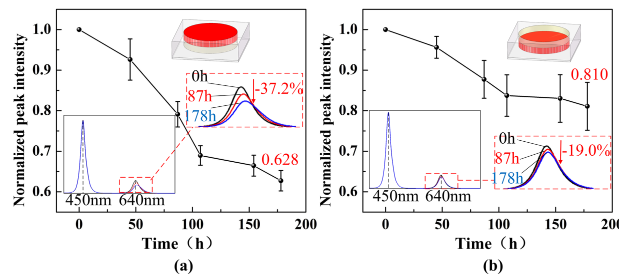

Fig. 8. Time evolution of the red light peak intensity of layered films with QDs/silicone film (a) upon and (b) below silicone film.

the blue light peak intensity was recorded shown as Fig. 5(a). It shows that the blue light peak intensity rarely changes, which proves that the stability of the bare LED chips is quiet well. For the silicone film, the blue light peak intensity was recorded shown as Fig. 5(b). It shows that the blue light peak intensity is reduced by 3.0%, which indicates that moisture has little effect on the stability of the silicone. For the phosphors/silicone film, the yellow light peak intensity was recorded shown as Fig. 5(c) and a 12.5% reduction of yellow light peak intensity was observed. For the QDs/silicone film, the red light peak intensity was recorded shown as Fig. 5(d). It shows the red light peak intensity is reduced by 54.0%, which is 4 times higher than that of yellow light peak intensity. From Fig. 5, it can be seen that the moisture stability of QDs is the key factor for determining the moisture stability of QDs-LEDs, so it is necessary to find solution to improve the moisture stability of QDs by optimizing the layered packaging structure.

In addition to the moisture, temperature could also induce thermal quenching of QDs and phosphors. To characterize the thermal stability of the QDs and phosphors in the experimental setup shown in Fig. 3(a), a new packaging structure with layered film embed in an enclosed glass container was used. In the new packaging structure, no moisture can penetrate the QDs and phosphors. So the failure of QDs and phosphors can be attributed to the influence of temperature. Fig. 6(a) shows the time evolution of normalized yellow and red light peak intensity of the new packaging structure at temperature of 50 °C. It shows that the yellow and red light peak intensity rarely changes with the aging time, which indicates that the thermal quenching of QDs and phosphors during the moisture stability characterization can be ignored. Fig. 6(b) shows the time evolution of normalized red light peak intensity of the QDs/silicone films at temperatures of 65 °C, 85 °C and 100 °C. It shows that the degradation of the red light peak intensity increases as the temperature increases.

Fig. 7 shows the time evolution of normalized yellow and red light peak intensity of layered films with QDs/silicone film upon and below the phosphors/silicone film. Two conclusions can be drawn from Fig.7. 1) The layered packaging structure with QDs/silicone film below the phosphors/silicone film can enhance the moisture stability of QDs-LEDs. The normalized red light peak intensity of layered film with QDs/silicone film upon phosphors/silicone film is reduced by 21.1%. However, the normalized red light peak intensity of layered film with QDs/silicone film below silicone film is reduced by 8.0%, which is 62.0% lower than that with QDs/silicone film upon phosphors/silicone film. This is because the upper layer insulates the moisture from the lower layer. 2) The normalized peak intensity of yellow light increases slightly for both two layered films. This is because the QDs and phosphors have a competitive relationship in the absorption-conversion of blue light. When the QDs fails, more light can be absorbed and converted by the phosphors.

The results in Fig. 7 show that the competition of blue light absorption-conversion process of QDs and phosphors would affect the optical performance of layered films. Considering that the failure of QDs is the main factor for determining the moisture stability of QDs-LEDs, the phosphors/silicone film is replaced with silicone film in the layered films to eliminate the influence of phosphors on the light absorption-conversion process of QDs. The new layered films can more accurately characterize the moisture stability of QDs in the layered packaging structure. Fig. 8 shows the time evolution of normalized red light peak intensity of layered films with QDs/silicone film upon and below the silicone film. It shows that the normalized red light peak intensity of layered film with QDs/silicone film upon silicone film is reduced by 37.2%. However, the normalized red light peak intensity of layered film with QDs/silicone film below silicone film is reduced by 19%, which is 49% lower than that of QDs/silicone film upon silicone film. Both the results shown in Fig. 7 and Fig. 8 indicate that placing the QDs/silicone at the down layer of layered packaging structure is better for ensuring the moisture stability of QDs-LEDs.

IV. Conclusion

In this letter, the moisture stability of QDs-LEDs with layered packaging structure in a high moisture environment with relative humidity of ~99.8% was experimentally investigated. The results show that the moisture stability of QDs is the main factors for determining the moisture stability of QDs-LEDs. Compared to the layered packaging structure with QDs/silicone film upon the phosphor/silicone film that reported in previous study, the layered packaging structure with QDs/silicone film below the phosphor/silicone film decreases the red light peak intensity degradation by ~62%, which indicates that layered packaging structure with QDs/silicone film at the down layer can enhance the moisture stability of QDs-LEDs.

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