第30卷　第1期　　发　光　学　报　　Vol. 30　No. 1
2009年2月　　CHINESE JOURNAL OF LUMINESCENCE　　Feb., 2009

Article ID: 1000-7032(2009)01-0019-06

Investigation on Improving the Extraction Efficiency of Power White LEDs with Slurry Method

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Abstract: Slurry method based on a phosphor suspension in a water-soluble photoresist was discussed. A conformal-coating phosphor layer was deposited on the surface of LEDs. The luminous performance of power white LEDs was found to be mainly depending on the concentration and ratio of ingredients in slurry and the structure of coating layer. In this paper, the parameters were investigated and some advices, which were suggested to improve the performance, were proven to be effective in our experiment. The aging testing of LEDs with this slurry method showed that the luminous flux was 95.95% of that of the beginning after the LED was lightened for 168 h at 700 mA.

Key words: white LEDs; slurry; extraction efficiency; packaging

CLC number: O482.31; TN312.8　　**PACC**: 7860F　　**Document code**: A

1 Introduction

LED is for light-emitting diode. The first blue GaN LED was invented in 1993[1] and subsequently white-LED in 1996 was fabricated. Advantages of LEDs include high brightness, reliability, low power consumption and long life[2,3]. Currently, LEDs play an important role in many applications including large area displays, automotive and aircraft lighting, traffic signals. LEDs will soon play a much larger role in the future of architectural lighting and general illumination[4~9]. As a result, more and more attentions had been paid to the LEDs industry by world wide governments and companies.

White light can be generated by LEDs with the one of three ways or approaches[10]. The first is through combining light of red, green to, and blue LEDs. The second approach is to use a UV LED emitter to excite red, green, and blue phosphors, as the same way of fluorescent lamps to generate white light. The most common approach for producing white LEDs is to use a broadband yellow-emitting phosphor such as YAG: Ce^{3+} which effectively absorbs 460 nm blue light of a blue LED chip and emits 560 nm yellow light. Nowadays, the typically phosphor coating process is that phosphor-containing epoxy is dropped on the surface of a blue LED chip. There are three disadvantages to the white LEDs fabricated with this method. First, the production efficiency is lower, which cannot fit the modern industrial production; second, the thickness of phosphor layer is non-uniformity, which introduce non-uniformity within the light spot of LED; third, the chromaticity deviation among LEDs is inevitable. In light of above issues, a conformal phosphor coating method[10~12] *i. e.* the slurry method was employed in our experiment, which firstly used for color CRT production. A conformal-coating phosphor layer covered LED chip emitting surface was realized by slurry method based on a self-developed phosphor suspension in a water-soluble photoresist.

2 Slurry Method

As a coating process, slurry method involves

Received date: 2008-05-18; **Revised date**: 2008-07-25

Foundation item: Project supported by the National High Technology Research and Development Program (863) of China (2006AA03A116); Application-based Research of Sichuan Province (2008JY0051)

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dipping, flowing and photo-development of a phosphor suspension in a water-soluble photoresist. A slurry comprised of polyvinyl alcohol(PVA), ammonium dichromate (ADC), deionized water and yellow phosphor particles($Y_3Al_5O_{12}$:Ce^{3+}) was prepared with certain proportion[11,13,14]. After the slurry layer was coated on the surface of blue LED chip and then dried in darkroom, the layer was exposed to blue light emitted from the LED chip as applied with direct current, a photochemical reaction included oxidation of the PVA and reduction of the ADC occurred and resulted in cross-linking between fragmented PVA chain. A desired pattern of phosphor layer (exposed area) was remained on the surface of LED chip after developed with hot water, which was schematically shown in Fig. 1.

Fig. 1 Schematic diagram of the slurry method for phosphor coating

The luminous performance of white LEDs fabricated by the slurry method depended on the concentration and ratio of ingredients in slurry, stand-time of slurry and packaging silicon layer after phosphor coating.

3 The Influence of ADC

Cr, which was dissociated from ADC, was important in increasing cross-linking, but it can contaminate the radiative recombination sites of some phosphors and quench light output[13]. The absorption spectrum of Cr^{3+} mainly has two wide bands: one was around 433.60 nm (corresponding to the $^4A_2 \rightarrow {}^4T_1$ transition of Cr^{3+}) and the other one was at about 620 nm (corresponding to the $^4T_2 \rightarrow {}^4A_2$ transition of Cr^{3+}) [15], as shown in Fig. 2.

Fig. 2 Absorption spectrum of Cr^{3+}

Because of the two wide absorption bands, especially the band of 433.6 nm which is close to the emission band of blue-LED, the luminescence efficiency of white LEDs with slurry method was restrainted and lower than that of LEDs with silicone packaging layer.

It was then suggested that the luminescence efficiency of white LEDs should increase by deceasing the concentration and usage of ADC on the slurry, *i. e.* Cr^{3+} in phosphor-dispersed layer.

Two experiment concerning on the ADC concentration in slurry were carried out to investigate its influence on the efficiency of LEDs.

3.1 Decreasing the Concentration of ADC at the Same Phosphor Quantity

The thickness of phosphor layer was kept to be the same in the case of the same yellow powder concentration in the slurry were applied. By reducing the ADC concentration in slurry its quantity can be decreased in the coating layer, and then, the luminous intensity of the white LEDs would be improved. Table. 1 shows the data of luminous intensity of LEDs with different concentration of ADC.

As shown in the table above, it is obviously that the luminous intensity of LEDs increase with the decrease of concentration of ADC in slurry. A conclusion can be made that the luminous intensity of LEDs will continually increase along with the further decrease of concentration of ADC. In table. 1, the correlated color temperature (CCT) and colorimetric chromaticity data of white LEDs were different because of their different exposure time, in other words, the CCT and colorimetric data of white LEDs were controlled by the exposure time.

Table 1 The luminous intensity data of LEDs coated slurry with different concentration of ADC

Sample	ADC CON. (Mass fraction)	Intensity (mcd)	CCT(K)	Coordinate-*x*	Coordinate-*y*
1	0.02	4 663	8 165	0.291 1	0.3173
2	0.02	4 567	8 569	0.287 3	0.313 9
3	0.10	3 850	7 114	0.302 4	0.336 5
4	0.50	2 213	7 058	0.303 6	0.334 9
5	0.50	2 000	-	0.253 9	0.243 3

3.2 Increasing the Concentration of Phosphor on the Same ADC Quantity

The thickness of phosphor layer would lessen with the increase of concentration of phosphor in the slurry. The reduced thickness of phosphor layer made the content of Cr^{3+} in phosphor layer decreased, which led more blue-light and yellow-light to come out from the device and enhanced the luminous intensity of white LEDs, as shown in Fig. 3.

Fig. 3 Contrast of the exposure time and luminous intensity of LEDs coated with two different slurries

The curve Ⅰ indicates the luminous intensity of LEDs coated with the slurry comprising 2.76 mg PVA and 0.02 mg ADC in 1 mL aqueous solution, as well as 250 mg phosphor (slurry Ⅰ) and curve Ⅱ indicates that of LEDs coated with the slurry consisting of 2.76 mg PVA and 0.02 mg ADC in 1 mL aqueous solution, as well as 100 mg phosphor. (slurry Ⅱ), as shown in Fig. 3. Generally speaking, the luminous intensity of the curve Ⅰ is higher or more intensive than that of the curve Ⅱ at the same concentration of ADC and PVA in slurry. This could be interpreted that the thickness of phosphor layer was thinner with higher concentration of phosphor, less blue-light and yellow-light was absorbed again, consequently leading to luminous intensity increasing. It can be concluded that the luminous intensity of white LEDs might increase through increasing the concentration of phosphor in slurry and lessening the exposure time.

4 The Influence of Stand-time

The adhesive strength of the phosphor dispersed in coating layer on the surface of blue LED chip was weak when there were many air bubbles in the slurry. The reason is that when fresh slurry was coated on the surface of LED chip, the phosphor layer was not uniform after these bubbles in the slurry broke. the fresh slurry was stood in darkroom for hours in order to release these bubbles and improve the adhesive strength. However, It was found that the luminous intensity of the LED with slurry which stood for longer time (for example one day) in darkroom was lower than that stood for 3 ~5 h, which might be due to the darkness reaction of polymer ingredients and more reduced Cr^{3+} of ADC in slurry. The luminous intensity of LED coated with the slurry of different stand-time was measured. As shown in Fig. 4, the ingredients in the slurry was 5.9 mg PVA and 0.1 mg ADC in 1 mL aqueous solution, as well as 250 mg phosphor.

Fig. 4 The luminous intensity of LEDs coated slurry with different stand-time

5 The influence of Silicon Gel Layer

After such processes as coating, exposure and developing, a proper thickness and uniform yellow phosphor layer was deposited on the surface of blue LED chip. The admixture mixed silicon gel A with B according to the same volume was coated on the LED which was already coated with phosphor particles. A layer of silicone admixture of two part A and B was introduced above the phosphor layer, then the gel layer was solidified in a oven at 120 ℃ for 2 ~ 2.5 h. Comparing LED, before and after silicone coating, the chromaticity and luminous flux were different in the test.

As shown in Fig. 5, the same color icons denote the colorimetric data of the same chip coated and uncoated with the silicon gel layer. The square and pentacle denote the colorimetric data of LED coated and uncoated silicon gel layer, respectively. The above figure show that the colorimetric value decrease, which mean the transfer output light to the short wavelength after white LEDs was coated with silicon gel layer. Namely, the hue of light of white LEDs moved forward to the blue-light zone.

At the same time, it was noticeable that the colorimetric data of white LEDs with different exposure time were varied. The closer to the blue-light zone the hue was, the lower luminous flux of white LEDs was. On the contrary, the closer to the yellow-light zone the hue was, the higher luminous flux

Fig. 5 The changes of the chromaticity of LED's emission

of white LEDs was. As shown in Table 2, the colorimetric data of all LEDs coated with phosphor particles decreased and the luminous flux increased after silicon gel was coated on LEDs. For the three LEDs marked by 〈1〉,〈2〉 and 〈3〉, uncoated silicon gel layer, their hues were all in yellow-light zone and their luminous flux was only 45 ~ 59 lm. Whereas, their colorimetric data were into white-light zone and their luminous flux increased greatly, about 79.4 ~ 84.9 lm, after silicon gel was coated on LEDs, corresponding to (1),(2) and (3); For the two LEDs marked by 〈4〉 and 〈5〉, uncoated silicon gel, their hues were all in white-light zone and their luminous flux was only 52 ~ 53 lm. However, the hues were in blue-light zone and their luminous flux increased in different extent after silicon gel was coated over LEDs, corresponding to (4) and (5). The phenomenon might have something with the refractive index of the silicon gel. When the silicon gel was not coated on the LED, the discrepancy of refractive index between phosphor layer and air was evident, so the angle of total reflection became small, which induced less blue light could be extracted from the white LEDs. More blue light was rebounded by phosphor particles, and converted into yellow light or absorbed by the yellow phosphor layer. As a result, more yellow light came out from the LED, which made the hue of light from the LED lean to the yellow-light zone and the luminous flux was low. After the LED coated phosphor particles was coated with silicon gel, the discrepancy of refractive index between phosphor layer and silicon gel layer was not too and the angle of total reflection was extended and more blue light could be extracted form LED, therefore, the hue of light from the LED was in the blue-light zone and the luminous flux was higher.

Table 2 The changes of the chromaticity and luminous flux of LEDs

Sample	〈1〉	(1)	〈2〉	(2)	〈3〉	(3)	〈4〉	(4)	〈5〉	(5)
Colorimetric data x	0.416	0.3496	0.417	0.353	0.38	0.2931	0.302	0.2233	0.282	0.2146
Colorimetric data y	0.518	0.4094	0.518	0.342	0.464	0.3084	0.328	0.1832	0.3	0.175
Luminous flux /lm	49.5	84.9	44.8	80.5	59	79.4	52	61.4	53	50.9

6　The Aging Process of White LED

When direct current was applied to the LED, their luminous flux would lessen gradually as the working time increased. As for white LEDs, the degradation speed was a significant guide line for its practicability and also a assess point of the technology. Only the luminous flux of white LEDs is still high after they were lighten for some time, the white LEDs could attained the practical demand. The white LEDs fabricated by slurry method, whose rated drive current was 350 mA, were applied 700 mA current in order to accelerate the aging process.

Fig. 6 illustrates the luminous flux of white LEDs as a function of aging time. Though the luminous flux of white LEDs decreased as the time increased, the degradation speed was slow. The luminous flux of the white LED marked by 1# was 95.95% of that of the beginning after the LED was lightened for 168 h at 700 mA direct current, and 2# was 79.26% of that of the beginning after the LED was lightened for 168 h at 700 mA. During 212 ~ 404 h, the luminous flux does not change.

Fig. 6　The test of luminous flux of power white-LEDs with slurry

7　Conclusion

The uniform and optimized thickness of yellow phosphor layer on the surface of blue LED chip was realized by the slurry method. The thickness and shape of the phosphor layer was controlled. The luminous intensity of white LEDs could be improved through decreasing the concentration of ADC or increasing the concentration of phosphor in the slurry. As a result of darkness reaction, the white LEDs coated with the slurry stood for one day or longertime had low luminous efficiency. Properly extending the exposure time, not only the hue of light from white LEDs coated with silicon gel player in white light zone, but also the luminous flux were improved greatly.

8　Acknowledgements

The authors would like to thank the support of the Ministry of Science & Technology of China and Sichuan Province

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基于粉浆法提高功率型白光 LEDs 的提取效率

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摘要: 讨论了基于水溶性感光胶的荧光粉的涂层技术,利用粉浆法,在蓝光 LED 芯片的表面获得了荧光粉平面涂层。证实了得到的白光 LED 的光提取效率与粉浆中各成份的浓度和相应的比例有关,并在实验的基础上,采用了一些切实切可行的措施来增加器件的光提取效率。得到的白光 LED 在 700 mA 加速老化 168 h 后,其光能量为初始时的 95.95%。

关 键 词: 白光 LEDs; 粉浆; 提取效率; 封装

中图分类号: O482.31; TN312.8 **PACC:** 7860F **文献标识码:** A

文章编号: 1000-7032(2009)01-0019-06

收稿日期: 2008-05-18; **修订日期:** 2008-07-25

基金项目: 国家"863"计划(2006AA03A116); 四川省应用基础研究基金(2008JY0051)资助项目

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