Microelectronics Reliability 54 (2014) 2849–2852

Contents lists available at ScienceDirect

Microelectronics Reliability

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

Direct correlation between reliability and pH changes of phosphors for white light-emitting diodes

Minho Choi, Ki Hyun Kim, Changhun Yun, Dai Hyoung Koo, Sang Bin Song, Jae Pil Kim *

Lighting Sources & Materials Research Center, Korea Photonics Technology Institute, 108, Cheomdan venture-ro, Buk-gu, Gwangju 500-779, Republic of Korea

ARTICLE INFO

Article history:
Received 6 March 2014
Received in revised form 21 July 2014
Accepted 21 July 2014
Available online 22 August 2014

Keywords:
Light-emitting diode (LED)
Phosphor
Reliability
Degradation

ABSTRACT

The reactivity of phosphor with water was investigated by measuring pH change, and the results are compared with long-term reliability test results as well as scanning electron microscope (SEM) and inductively coupled plasma optical emission spectroscopy (ICP-OES) results. We found that the slope of pH change strongly depends on phosphor composition and represents a long-term reliability test result induced by phosphor in an LED package.

1. Introduction

Recently, incandescent light and fluorescent light have been rapidly replaced with light-emitting diode (LED) due to its many advantages such as semi-permanent lifespan, low electric power consumption, compact size and absence of toxic mercury [1–3]. White LEDs is generally manufactured by combining yellow phosphor and a blue LED chip [4,5]. However, it has low color rendering index due to lack of red or green components [1,6]. In order to solve such a problem, white LED is manufactured by applying red, green and blue phosphors on ultraviolet chips, or by applying red and green phosphors on blue LED chips [7–13]. One can notice that phosphors are one of the main materials determining properties of a white LED [14].

Reliability of LED is evaluated for at least 1000 h up to 5000 h with stress factors such as temperature and humidity. Such a long evaluation time needs many human and material resources as well as time consumption during the measurement. Also, there would be a high possibility that unexpected artificial factor influences on the test result. As evaluation time longer, the possibility gets higher. Furthermore, the long evaluation time slows down the speed of new phosphor development due to time consuming feedback process.

Main factors which influence on the reliability of phosphor are heat, humidity and light. These factors reduce quantum efficiency of phosphor, and as a result, variation of color coordinate and reduction of optical power of white LED occur [15–20]. It has been reported that heat leads to quantum efficiency reduction and emission wavelength shift of phosphor [17,18,20]. However, the influence of humidity on phosphor is not well investigated [21].

This paper reports a method to evaluate the reliability of phosphors in a short time. We have measured the change of pH in deionized water after soaking phosphors into it. And the results are compared to long-term reliability of LED package fabricated with the same phosphors.

2. Experiment

To fabricate an LED package with phosphors, we used a 45 mil chip with 458 ± 2 nm emission band (Epistar in Taiwan) and a 9080 package (9 mm in width x 8 mm in length, Enomoto in Japan). OE-6650 silicone (refractive index = 1.54, Dowcorning in USA) was mixed with 5 wt% of $Y_3Al_5O_{12}$:Ce phosphor (emission band: 555 nm, Nemoto in Japan, hereafter, phosphor A), silicate-type $(Sr,Ba)_2SiMgO_4$:Eu phosphor (emission band: 521 nm, Force4 in Korea, hereafter, phosphor B), and Nitride-type $(Sr,Ca)_2Si_5N_8$:Eu phosphor (emission band: 620 nm, Intematix in USA, hereafter, phosphor C), respectively. Then, it was cured in a convection oven for 1 h at 70 °C and for 2 h at 150 °C. Finally the prepared LED package was placed on a metal core printed circuit board (PCB) to make an LED device. The optical properties of fabricated LEDs were measured at 100 mA of electrical current with a spectrometer (Instrument system, CAS-140CT) after storing in a chamber with high-temperature (85 °C) or high-temperature and high-humidity (85 °C/RH 85%) as a function of exposure time in the chamber.

* Corresponding author.
E-mail address: jpkim@kopti.re.kr (J.P. Kim).

http://dx.doi.org/10.1016/j.microrel.2014.07.141

During storage, the samples are operated at 100 mA of electrical current.

To investigate reactivity of phosphors against water, 0.01 g of A, B and C phosphors was inserted to a flask containing 40 ml of deionized water, respectively, then the evolution of pH in the solution was measured with a pH meter (pH 6000, Euteck instruments in Singapore), while stirring at 120 rpm and 30 °C. The phosphors were not coated to protect from humidity before soaking into water. To analyze the reactions during the evolution of pH in the solution, inductively coupled plasma optical emission spectroscopy (ICP-2OES, Varian) was measured. Furthermore, scanning electron microscope (SEM) images were taken to observe the changes of the phosphor surface.

3. Results and discussion

To check the reliability of phosphor in LEDs, LED package fabricated with phosphor A, B or C (hereafter, LED device A, B or C, respectively) is operated under high-temperature (85 °C) and high-temperature and high-humidity (85 °C/RH 85%) condition. Fig. 1(a) and (b) shows the relative luminous fluxes as a function of exposed time under the ambient condition of 85 °C and 85 °C/RH 85%, respectively. LED devices encapsulated without phosphors are measured as a reference to exclude the other factors induced by an LED chip, an encapsulant, a lead frame, etc. Under the high-temperature condition, the relative luminous flux of the reference device exceeds 100% at early stage due to so called "aging effect" [22].

In the 85 °C-chamber, the drops of the luminous flux from device A and B are almost overlapped, whereas they are well separated under the condition of 85 °C/RH 85%. More accurately, the luminous flux in device A does not change regardless of the ambient condition, although the light emission in device B decreases faster under high-temperature and high-humidity condition. In device C, there is a distinguished decrease in the luminous flux in both conditions for the reliability test. Especially, under the condition of 85 °C/RH 85%, device C shows a rapid decrease within initial 270 h, and then the dropping rate slows down. We suppose that this is because the surface of phosphor C is rapidly degraded by water, then the degraded layer hinders water permeation and protects the inside of the phosphor. From these results, one can easily notice not only that the water vapor strongly influences on the degradation of luminous flux in LEDs but also that the reliability test of LEDs strongly depends on

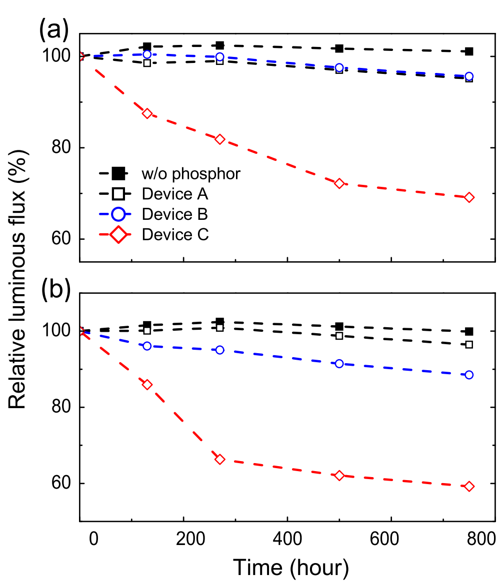

Fig. 1. The plot of relative luminous flux vs. exposed time under (a) 85 °C- and (b) 85 °C, RH 85%- ambient conditions using the blue LED without phosphor (w/o phosphor, filled rectangles) and the white LEDs based on three different phosphors: phosphor A (device A, open rectangles), phosphor B (device B, open circles) and phosphor C (device C, open rhombuses).

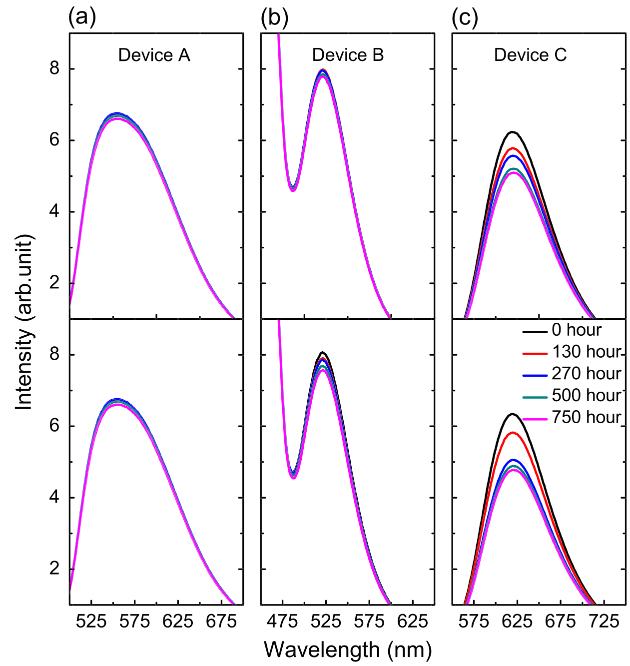

Fig. 2. The normalized emission spectra of white LEDs using (a) phosphor A (device A), (b) phosphor B (device B), and (c) phosphor C (device C) depending on the operating time under 85 °C- (upper curves) and 85 °C, RH 85%- (lower curves) ambient conditions, respectively.

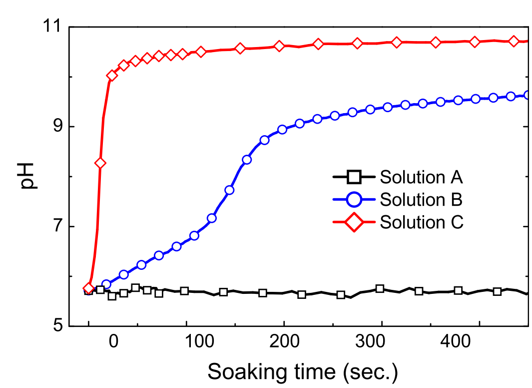

Fig. 3. The pH curves of the deionized water solution with phosphor A (rectangles), phosphor B (circles) and phosphor C (rhombuses) according to the soaking time.

Table 1
Analytical results for ion concentrations in the water solution after the soaking test of three different phosphors (phosphor A, B and C) by inductively coupled plasma optical emission spectroscopy (ICP-OES).

Element	Phosphor A	Phosphor B	Phosphor C
Sr	ND	6.8 ppm	27.4 ppm
Ba	ND	13.4 ppm	ND
Al	ND	ND	ND
Y	ND	ND	ND
Si	ND	ND	ND
Ce	ND	ND	ND
Eu	ND	ND	ND

"ND" corresponds to the not detected.