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Incorporation of anatase TiO_2 particles into silicone encapsulant for high-performance white LED

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ABSTRACT

The optical performances of correlated color temperature (CCT) uniformity, luminous flux, and reliability of cool white light-emitting diodes (LEDs) with diffuser additives, including anatase TiO_2, rutile TiO_2, and ZrO_2 particles, are comparatively evaluated on the basis of approximate CCT of 7200 K. Among the applications of such metal oxides, the incorporation of anatase TiO_2 contributes to relevant white LED having the most enhanced luminous flux and a reduced CCT deviation of 7.1 and 95.2%, respectively, with reference to the performances, deriving from the bare white LED at 350 mA. Additionally, the anatase TiO_2-loaded white LED exhibits a steady lumen output for at least 2000 h.

1. Introduction

The white light source, originating from a phosphor-converted white light-emitting diode (LED), has positively impacted on the life of human beings, such as lighting, since 1996 [1,2]. This kind of light source is worth using extensively due to the benefits of relevant white LED, including easy preparation and cost-effective manufacturing process, with reference to the white lighting, developed by integration of multiple LEDs with various wavelengths, i.e., RGB [3]. Owing to the phosphor-converted white LED basically composed of a blue LED chip and yellow phosphor particles, a common issue raised is the inhomogeneous correlated color temperature (CCT), namely yellow ring phenomenon, of light spot projected by white LED [4]. A promising strategy, adopted for improving the CCT uniformity, is to include a diffuser additive in the encapsulant of white LED [5].

In recent years the submicron particles of metal oxides, such as TiO_2 and ZrO_2, have served as potential diffuser materials [6,7]. It was reported that TiO_2 particles exhibit a remarkable light scattering ability in favor of the reduction of angular CCT variance of its white LED [6]. Moreover, the enhancements in both CCT uniformity and luminous flux of the white LED with ZrO_2 particles were demonstrated [7]. Thus, we have comparatively evaluated the optical performances of angular-dependent CCT, luminous flux, and reliability of the white LEDs employing various diffusers, including anatase TiO_2, rutile TiO_2, and ZrO_2 particles, in this article. Most importantly, these investigations were conducted on the basis of the corresponding white LEDs having nearly the same CCT.

2. Experimental

TiO_2 particles with crystalline phases of anatase and rutile were confirmed by X-ray diffraction patterns (Fig. S1, Supporting Information). ZrO_2 particles were commercial products from MeiTek Inc., Taiwan. The anatase TiO_2, rutile TiO_2, or ZrO_2 particles having average diameters of about 300 nm were incorporated into the silicone slurry, containing 3.0 wt% of phosphor Ce^{3+}-doped $Y_3Al_5O_{12}$ (YAG:Ce) powder. We further filled the space of a lead frame, equipped with a GaN-based blue LED chip, with the composite of metal oxide/YAG:Ce/silicone by using a dispenser. The white LED was finally obtained (Fig. 1a). The LED chip has an emission peak wavelength of 450 nm under current injection. The morphology of the metal oxide of encapsulating composite should be presented in the form of aggregations due to the formations of secondary particles, resulting from the chemical incompatibility between metal oxide with hydrophilic surface and silicone-based encapsulant with hydrophobic property. It was suggested that the consistency in degrees of anatase TiO_2, rutile TiO_2, and ZrO_2 aggregations can be well aligned due to their encapsulating composites, totally prepared using the same manufacturing process. Thus we considered that these aggregations had less to do with the disturbance to performance competition between

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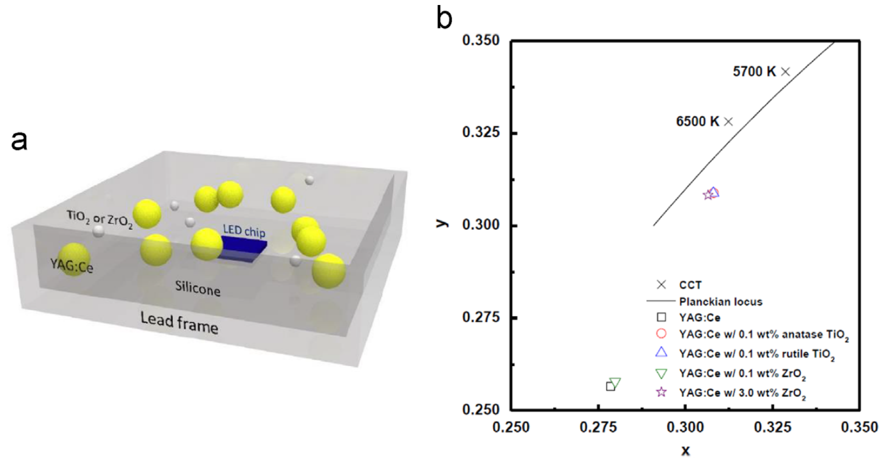

Fig. 1. (a) Illustration of white LED with YAG:Ce particles and diffusers. (b) CIE 1931 chromaticity coordinates of white LEDs at 350 mA.

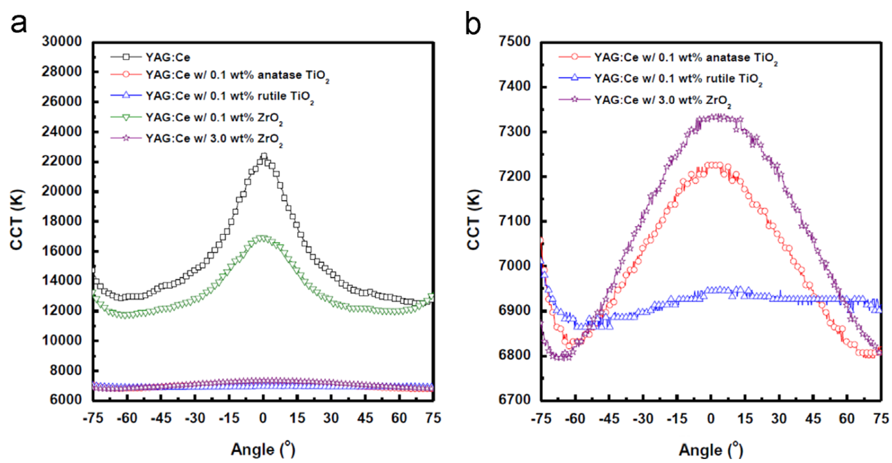

Fig. 2. (a) Angular CCT distributions of white LEDs at 350 mA; (b) large-scale Y-axis of (a).

relevant white LEDs in this work. An integrating sphere was utilized to characterize the optical properties of the samples.

3. Results and discussion

In the absence of diffuser, the bare white LED with input current of 350 mA delivered high CCT of about 15000 K in relation to its color coordinate (0.278, 0.257), found close to the blue domain [8] of CIE 1931 chromaticity diagram (Fig. 1b). This means abundant blue light is generated from such a white LED. By adding 0.1 wt% diffusers, the coordinates of corresponding white LEDs, shifting toward yellow region [8], were observed in both cases of anatase and rutile TiO_2 but in the case of ZrO_2 (Fig. 1b). It ultimately made the white LEDs, using TiO_2, give lower CCTs of ca. 7200 K, with reference to the CCT of bare white LED. The decreased CCTs reveal that the light scattering abilities of anatase and rutile TiO_2 benefit the blue light-promoted YAG:Ce absorption as well as conversions of blue into yellow light. However, in Fig. 1b, the ZrO_2 content needed to be increased from 0.1 to 3.0 wt% for achievement of the same color coordinate of its white LED in comparison with the cases of anatase and rutile TiO_2. The requirement of high ZrO_2 content can be explained by the intrinsically superior light scattering property of TiO_2 than that of ZrO_2. Moreover, the absorption of blue light through diffusers was considered as a minor effect on the performances of white LEDs due to the emission peak wavelength (@450 nm) of the LED chip is inconsistent with the characteristic absorption peaks of anatase TiO_2, rutile TiO_2, and ZrO_2 (Fig. S2, Supporting Information).

Table 1
ΔCCT and luminous flux of white LEDs containing 3.0 wt% YAG:Ce and various diffusers at 350 mA. Each value is averaged over three independent samples.

White LEDs	ΔCCT (K)	Luminous flux (lm)
YAG:Ce	9517 ± 514	112.4 ± 2.0
YAG:Ce w/ 0.1 wt% anatase TiO_2	457 ± 50	120.4 ± 1.1
YAG:Ce w/ 0.1 wt% rutile TiO_2	186 ± 45	110.6 ± 0.7
YAG:Ce w/ 0.1 wt% ZrO_2	3792 ± 1193	115.3 ± 2.3
YAG:Ce w/ 3.0 wt% ZrO_2	551 ± 80	119.6 ± 1.6

To further have an insight into the light scattering effects of the diffusers, the angular CCT distributions of white LEDs were characterized in Fig. 2a and b. The CCT deviation (ΔCCT) was estimated using following relation [9] and then summarized in Table 1.

$$\Delta CCT = CCT_{max} - CCT_{min}, \qquad (1)$$

where CCT_{max} and CCT_{min} are maximum and minimum CCT, respectively. Fig. 2a exhibits the bare white LED renders a higher CCT around 0° than around −75° or 75° as well as a ΔCCT of 9517 ± 514 K (Table 1) due to the LED chip emitting a large amount of light in the direction of top surface of chip at 350 mA. In Fig. 2a, the CCT divergences were reduced for all white LEDs, made of diffusers, because of their efficient light scattering. In particular the white LEDs based on 0.1 wt% anatase TiO_2, 0.1 wt% rutile TiO_2, and 3.0 wt% ZrO_2 presented nearly the same trend in CCT distribution (Fig. 2a) in accordance with their color coordinates observed in Fig. 1b. It is obviously seen that the white LED with 0.1 wt% rutile TiO_2 minimizes the CCT divergence (Fig. 2b) and gives the smallest ΔCCT of 186 $\pm$ 45 K (Table 1) among foregoing three cases, thereby implying the rutile TiO_2 owns the best light scattering ability. The better ability of rutile TiO_2, with reference to the ability of ZrO_2, results from the difference in inherent properties of materials between the TiO_2 and the ZrO_2. Additionally, the light scattering characteristic of rutile TiO_2, which is preferable than that of anatase TiO_2, has been reported [10]. Consequently, the sequence of the diffusers with reference to the light scattering performance is 0.1 wt % rutile TiO_2 > 0.1 wt% anatase TiO_2 > 3.0 wt% ZrO_2 > 0.1 wt% ZrO_2 (Table 1).

Nevertheless, the white LED with rutile TiO_2 generated the lowest luminous flux of 110.6 $\pm$ 0.7 lm among the cases of diffusers and bare condition (Table 1). We reason that such a reduction may be attributed to the exceptional light scattering of rutile TiO_2 facilitating the reabsorption of backscattering light by LED chip [9]. Compared to the case of rutile TiO_2, the white LEDs with 0.1 wt% anatase TiO_2 and 3.0 wt% ZrO_2 gave significant improvements in luminous flux of 120.4 $\pm$ 1.1 and 119.6 $\pm$ 1.6 lm, respectively (Table 1), because of the retardation of the reabsorption, resulting from backscattering light, for LED chip. Our results indicated that the rutile TiO_2 gave the best scattering ability. This extraordinary scattering can facilitate the excitation of YAG:Ce in the white LED with rutile TiO_2. However in the meantime it has more chances to make the photons return back to the LED chip, with reference to the cases of anatase TiO_2 and ZrO_2. In other words, the backscattering light is reduced for anatase TiO_2- or ZrO_2-loaded white LED.

Moreover, a greater lumen was acquired in the case of 0.1 wt% anatase TiO_2 than in the case of 3.0 wt% ZrO_2. The explanation to this was made by the variations in the refractive indexes (RI) of encapsulants, comprised of multiple materials, as follows [11]:

$$RI = \nu_1 RI_1 + \nu_2 RI_2, \quad (2)$$

where ν represents the concentration of material. It was reported that the RI of encapsulant can be effectively modified with introduction of TiO_2 [12,13] or ZrO_2 [14]. Although the RI of anatase TiO_2 (2.5) is slightly higher than the RI of ZrO_2 (2.2), the ν of 0.1 wt% TiO_2 is 30 times lower than that of 3.0 wt% ZrO_2. Therefore, we regard the ν of diffuser as the dominant factor on the final RI of encapsulant. Accordingly, the RI of the encapsulant, majorly containing 0.1 wt% anatase TiO_2, was somewhat lower than that of 3.0 wt% ZrO_2-based encapsulant. A low RI of encapsulant leads to a small RI contrast between encapsulant and air (RI_{air} = 1), thereby reducing the chance of total internal reflection at the encapsulant/air interface. The light can thus escape from the encapsulant more easily. Although the difference in RI at the interface between 0.1 wt% anatase TiO_2-based encapsulant and LED chip (RI_{GaN} = 2.4) was therefore larger than that at the 3.0 wt% ZrO_2-based encapsulant/LED interface, the impact of total internal reflection was dominated by the encapsulant/air interface due to the reasons as follows. The first reason is the extensively planar surface of encapsulant/air interface. Thus, the light can be easily trapped by the encapsulant at large viewing angles. The second is the presence of three-dimensional, chip-shaped encapsulant/LED interface, thereby contributing to easy extraction of the photons, deriving from the chip. Eventually, a higher 120.4 $\pm$ 1.1 lm was produced by white LED with 0.1 wt% anatase TiO_2 in comparison to the case of 3.0 wt% ZrO_2 (119.6 $\pm$ 1.6 lm) (Table 1).

The scattering effect can lead to low transmittance of the encapsulant, simply consisting of silicone and TiO_2, but it can make the blue photons, deriving from LED chip, have more chances to excite the YAG:Ce particles as well as lumen enhancement for packaged white LED using TiO_2. Thus we found that white LED based on 3.0 wt% YAG:Ce and 0.1 wt% anatase TiO_2 gave an improved luminous efficacy of 7.1% at 350 mA, with reference to the performance of white LED containing 3.0 wt% YAG:Ce. According to comparable particle sizes (ca. 300 nm) and identical concentrations (0.1 wt%) of anatase TiO_2, rutile TiO_2, and ZrO_2 for white LEDs, the significant differences in corresponding ΔCCT and luminous flux (Table 1), attributing to the scattering effects, rely on the fact that the inherent characteristics of metal oxide are crucial to the optical performances of its white LED. While 5.0 wt% YAG:Ce was merely included in the encapsulant, the corresponding white LED, injected with 350 mA, delivered 128.7 $\pm$ 2.6 lm at the color coordinate of (0.315, 0.322), which was roughly the same as the coordinates obtained in the cases of 0.1 wt% anatase TiO_2, 0.1 wt% rutile TiO_2, and 3.0 wt% ZrO_2.

In Fig. 3a, the lumen intensity of white LEDs with diffusers maintained a succession of 0.1 wt% anatase TiO_2, 3.0 wt% ZrO_2, and 0.1 wt% rutile TiO_2 in the range of 20 and 700 mA. At 700 mA, the difference in lumens between the cases of anatase and rutile TiO_2 increased with respect to those differences at lower driving currents (Fig. 3a). This may be attributed to the backscattering light of white LED with rutile TiO_2 taking place dramatically at high input currents, thus resulting in large numbers of photons, reabsorbed by LED chip. Fig. 3b shows the white LEDs applying 0.1 wt% anatase TiO_2 and 3.0 wt% ZrO_2, giving unfailing performances, are of 2000 hours'

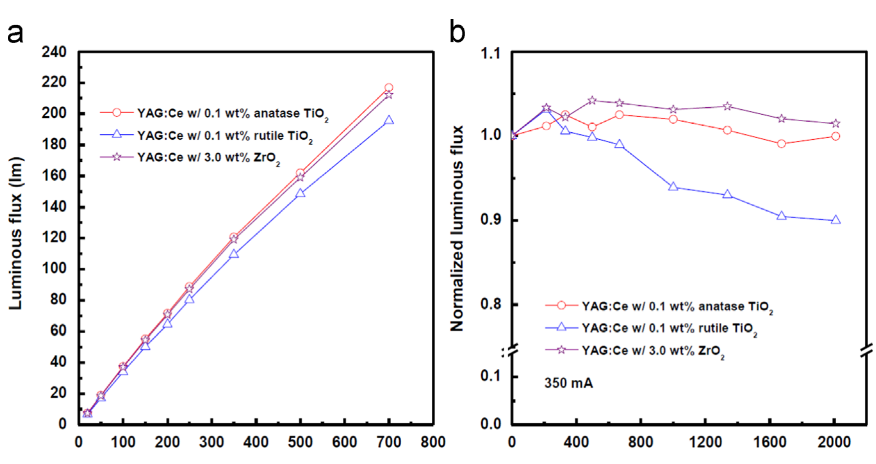

Fig. 3. (a) Luminous flux of white LEDs as a function of driving current. (b) Reliability tests of white LEDs, continuously injected with 350 mA, in a period of 2000 h.

durations. On the other hand, a relative lumen degradation of 10% was obtained for rutile TiO_2-loaded white LED in such a period of aging time (Fig. 3b). We ascribed the decay to the following two reasons. One is the reabsorption of abundant backscattering light, deriving from the extraordinary light scattering ability of rutile TiO_2 particles. The other reason is that large quantities of YAG:Ce particles are excited because a large number of photons, originating from the LED chip, are dramatically scattered by rutile TiO_2. This may lead to lots of heat productions, resulting from Stokes shift of YAG:Ce. The accumulation of heat can result in thermal degradation of rutile TiO_2/YAG:Ce/silicone composite more easily. Consequently, the lumen output of white LED using rutile TiO_2 decayed gradually as the aging time increased in this work. However, the thermal degradation barely impacts on the reliabilities of white LEDs with anatase TiO_2 and ZrO_2 for long-term duration of 2000 h owing to relatively ordinary scattering abilities of anatase TiO_2 and ZrO_2 (Fig. 3b).

4. Conclusions

The anatase TiO_2 particles, having moderate degree of light scattering, are capable of contributing to improved CCT uniformity and luminous flux of its cool white LED at the same time in contrast to the negative effect on lumen enhancement, brought from the white LED with rutile TiO_2. The reliability tests reflect the fact that both anatase TiO_2 and ZrO_2 are favorable for obtaining highly stable white LEDs. In terms of economic benefit, the consumption of 0.1 wt% anatase TiO_2 incorporation is saved for achieving the high-performance of corresponding white LED, as compared with the white LED based on highly doping concentration of 3.0 wt% of ZrO_2 particles.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.matlet.2014.12.134.

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