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Improvement in uniformity of emission by ZrO_2 nano-particles for white LEDs

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Abstract
The high luminous efficiency and superior uniformity of angular-dependent correlated color temperature (CCT) white light-emitting diodes have been investigated by ZrO_2 nano-particles in a remote phosphor structure. By adding ZrO_2 nano-particles with silicone onto the surface of the phosphor layer, the capability of light scattering could be enhanced. In particular, the intensity of blue light at large angles was increased and the CCT deviations could be reduced. Besides, the luminous flux was improved due to the ZrO_2 nano-particles with silicone providing a suitable refractive index between air and phosphor layers. This novel structure reduces angular-dependent CCT deviations from 1000 to 420 K in the range of $-70°$ to $70°$. Moreover, the enhancement of lumen flux was increased by 2.25% at a driving current 120 mA, compared to a conventional remote phosphor structure without ZrO_2 nano-particles. Consequently, the ZrO_2 nano-particles in a remote phosphor structure could not only improve the uniformity of lighting but also increase the light output.

(Some figures may appear in colour only in the online journal)

1. Introduction

In recent years, the advancement of solid-state lighting (SSL) has offered great potential to replace general lighting and illumination devices with high-power white light-emitting diodes (WLEDs) [1, 2]. One of the most promising methods to fabricate WLEDs is combining a blue LED chip with a $Y_3Al_5O_{12}$ (YAG) phosphor to produce white light, which is also known as phosphor-converted white light-emitting diodes [3]. This method offers high white-light efficiency and low cost, and is currently the most successful technology in SSL. Although this method is very popular, it still suffers color disharmony and low light extraction between air and the phosphor.

Today, pursuing high luminous efficiency by increasing light extraction has been extensively developed [4, 5]. Novel packaging methods, such as a hemi-spherically shaped encapsulation [6] and the ELiXIR pcLEDs architecture with internal reflection have been demonstrated to enhance the light extraction [7]. Even though we can improve light extraction by a properly designed package, the phosphor-emitting yellow photons inevitably go back to the package, and a significant portion would be lost within the package, thus decreasing the overall efficiency [8]. To solve this backscattering problem, one can separate the phosphor layer from the chip to suppress the re-absorption. Hence, a different phosphor structure, such as the ring-remote structure and scattered photon extraction (SPE), are designed to address this issue [9, 10].

The previous study indicated that the remote phosphor structure has higher luminous efficiency than conventional phosphor dispensing. However, during the fabrication of the remote phosphor structure, the concave encapsulant surface

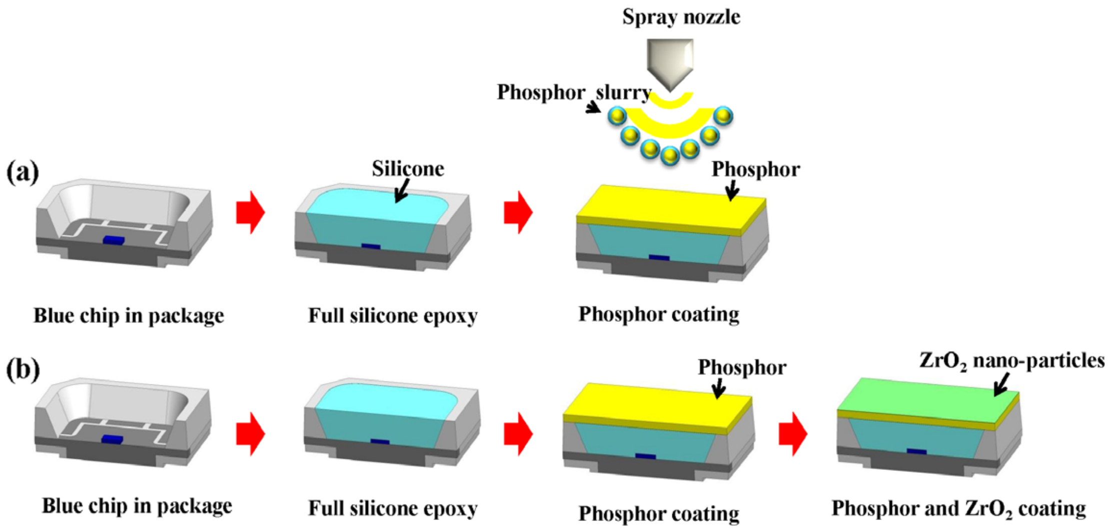

Figure 1. Schematic diagram of process flow charts (a) without; (b) with ZrO_2 nano-particles remote phosphor structure.

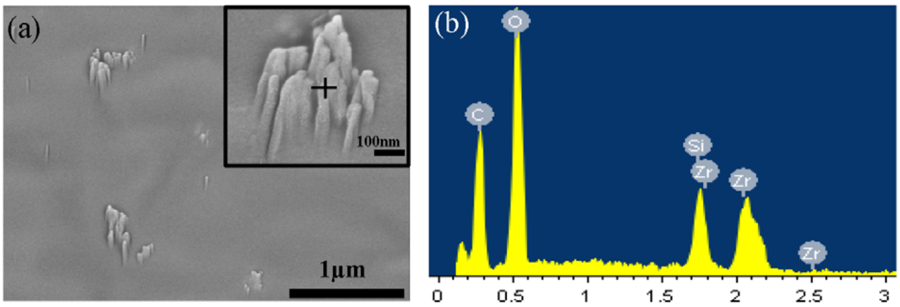

Figure 2. (a) A cross-sectional view of the SEM image of ZrO_2 nano-particles in silicone encapsulant. (b) The energy dispersive spectrometer (EDS) result was taken by a JEOL JEM-2100F system.

leads to a non-uniform phosphor thickness [11]. On the other hand, the angular-dependent optical path of blue light photons in this remote phosphor structure often leads to inhomogeneous excitation and a yellow ring appears at the perimeter of the device.

In this study, we use ZrO_2 nano-particles to improve the uniformity of the correlated color temperature (CCT) distribution in remote phosphor WLEDs. The ZrO_2 nano-particles could provide a superior scattering capability for the light. As a result, the intensity of blue light at large angles and the uniformity of CCT could be enhanced. Furthermore, the luminous flux could be enhanced by a ZrO_2 layer due to the refractive index gradient between air and phosphor layers.

2. Experimental details

Figure 1 illustrates the process flow charts of the experiment. The samples with remote phosphor structures are fabricated by the following steps: (1) blue LED chips, with size 24 mils square and peak emission wavelength of 450 nm, are placed in the plastic lead-frame package. The radiant fluxes of bare blue LED chips were 95 mW at a driving current 120 mA. (2) The transparent silicone is filled into the lead frame by dispensing and cured at 150 °C for 1 h. (3) The phosphor powders are combined with silicone binder and alkyl-based solvent to form a phosphor-suspension slurry. The pulse spray coating with interval control can improve phosphor slurry uniformity, as was previously demonstrated [12]. The $Y_3Al_5O_{12}$ (YAG) phosphor is used in this experiment with a particle size is about 12 μm. Then, the phosphor slurry is sprayed onto the surface of transparent silicone to form the conventional remote phosphor, as shown in figure 1(a). The fabrication of the ZrO_2 nano-particles in the remote phosphor structure differs from the conventional remote phosphor structure only in the final step, as shown in figure 1(b). The ZrO_2 nano-particles are mixed with silicone binder and an alkyl-based solvent and sprayed onto the surface of the phosphor layer, with the concentration of ZrO_2 nano-particles being 5%. The LED is picked with the same color temperature and color chromaticity coordinate for comparison at a driving current 120 mA. In order to inspect the experimental result of the ZrO_2 nano-particles in the silicone encapsulant, we also took the cross-sectional scanning electron microscopic (SEM) image, which shows the dimension of ZrO_2 nano-particles to be around 300 nm, as shown in figure 2(a). The element of ZrO_2 nano-particles with silicone encapsulant was analyzed by energy dispersive spectrometer (EDS), as also shown in figure 2(b) image. We can confirm the existence of Zr and O elements in the silicone encapsulant.

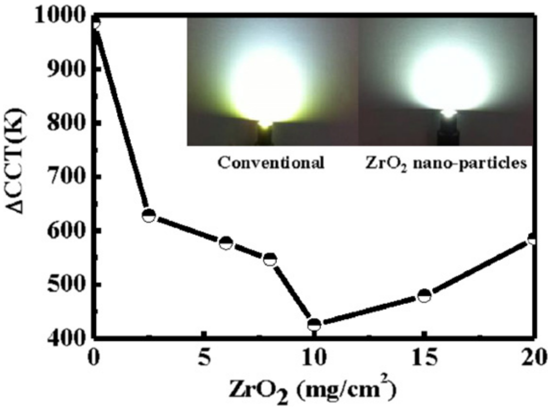

Figure 3. The CCT deviation of different weight of ZrO_2 layer in remote phosphor.

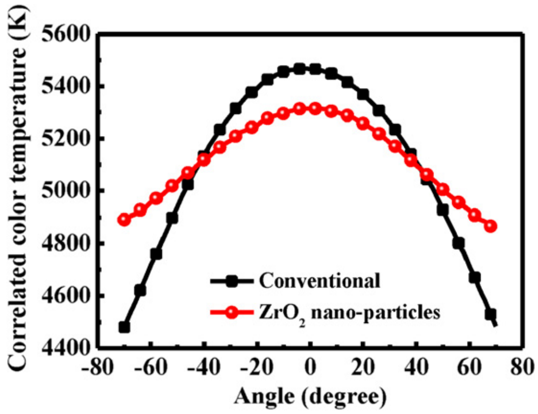

Figure 4. The angular-dependent correlated color temperature of conventional and ZrO_2 nano-particles remote phosphor.

3. Results and characterization

In general, the angular-dependent CCT uniformity could be defined by the maximum CCT minus minimum CCT. Different weights of ZrO_2 nano-particles with a silicone layer on the remote phosphor structure are fabricated to optimize the CCT deviation, as shown in figure 3. It is clear that the lowest CCT deviations and optimal weight of ZrO_2 nano-particles are exhibited at 10 mg cm^{-2}, which can obtain a 58% improvement compared to the conventional remote phosphor structure. The inset picture in figure 3 shows the far-field images for conventional and ZrO_2 nano-particles remote phosphor structures. With the scattering characteristic of ZrO_2 nano-particles, the blue and yellow light could be distributed uniformly. However, more ZrO_2 nano-particles than 10 mg cm^{-2} would influence the CCT deviations, but it still has better performance than the conventional remote phosphor structure. In the results, the remote phosphor structure with ZrO_2 nano-particles of 10 mg cm^{-2} could not only improve the uniformity of angular-dependent CCT, but also increase the luminous flux.

The angular-dependent CCT of the conventional and ZrO_2 nano-particles remote phosphor structures are measured and the weight of the ZrO_2 layer is 10 mg cm^{-2}, as shown in figure 4. It is clear that the angular-dependent CCT deviation of conventional and ZrO_2 nano-particles remote phosphor structures are improved from 1000 to 420 K in the range −70° to 70°. The conventional remote phosphor structure has an inferior angular-dependent CCT deviation due to blue light at a large angle being trapped and reflected in the phosphor layer. Therefore, extraction of blue light at a large angle is limited, which leads to ineffective color mixing of blue and yellow light. The ZrO_2 nano-particles with silicone on the surface of the phosphor layer have a smoother angular-dependent CCT distribution, because the ZrO_2 nano-particles could provide an effective scattering capability to improve the ratio of yellow to blue light at large angles. More detailed experiments and an explanation will be described in the next paragraph. The current-dependent luminous flux in the conventional and ZrO_2 nano-particles remote phosphor structures with a weight of 10 mg cm^{-2} are shown in figure 5. The CCT for both remote phosphor structures as fabricated are almost the same, 5010 and 5097 K at a driving current 120 mA. Furthermore, it is noticeable that the luminous flux of the ZrO_2 nano-particles structure increases by 2.25% at a driving current 120 mA. With the ZrO_2 nano-particles layer, the difference of refractive indices between interfaces can be reduced, and the light extraction can be increased. Because the refractive index of ZrO_2 nano-particles with silicone is about 1.5 and that of the phosphor is about 1.8, the ZrO_2 nano-particles with silicone could provide a refractive index gradient between air and phosphor layers.

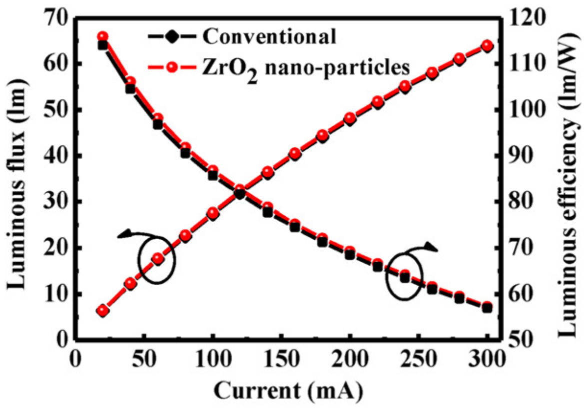

Figure 5. The luminous flux of the conventional and ZrO_2 nano-particles remote phosphor structures.

To understand the scattering capability of different weights of ZrO_2 nano-particles with silicone layer in the visible region, we measured the total transmittance and the non-specular transmittance (also known as diffractive transmittance) and calculated the haze parameter using the following expression [13]:

$$\text{Haze intensity} = T_{\text{diffraction}}/T_{\text{total}} \times 100\% \quad (1)$$

where $T_{\text{diffraction}}$ is the diffractive transmittance (not including the zero-order diffraction), T_{total} was the total transmittance, From the equation (1) above, the wavelength-dependent haze of the silicone layer with and without the ZrO_2 nano-particles

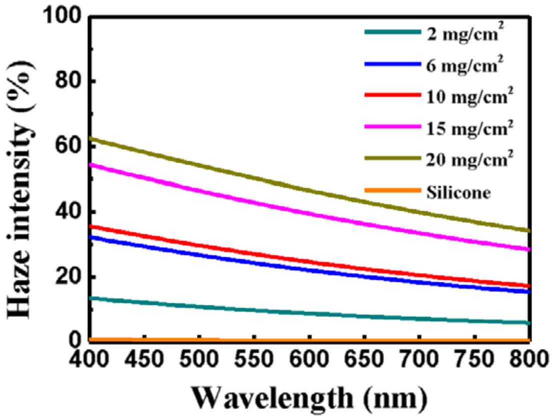

Figure 6. The measured wavelength-dependent haze intensity with only silicone and with different weights of ZrO_2 nano-particles.

are presented, as shown in figure 6. It is clear that the haze of the silicone-only layer is almost zero, and increases as the increase of weight of ZrO_2 nano-particles. The improvement of angular-dependent CCT deviation could be attributed to the scattering capability of ZrO_2 nano-particles. The higher haze intensity might be related to better scattering capability.

To understand the angular-dependent scattering intensity of different ZrO_2 nano-particle sizes for blue light and yellow light, the full-field finite-difference time-domain (FDTD) simulation is employed to demonstrate the effect on the CCT uniformity and light output with different ZrO_2 nano-particle sizes. In the simulated conditions, the refractive index of ZrO_2 nano-particles with silicone is about 1.5, and the concentration of ZrO_2 nano-particles is 5%. It was found that the ZrO_2 nano-particle of 400 nm has a better angular-dependent scattering intensity than other sizes in both blue (450 nm) and yellow (560 nm) incident light, as shown in figures 7(a) and (b). Although the higher scattering effect could lead to good CCT uniformity, the transmittance of blue and yellow light in the normal direction should be considered. From our measurement of pure ZrO_2/silicone film, we could see a steady rising trend of absorption when the film grows thicker. This absorption can account for 5%–15% of light in the 300 nm ZrO_2 particle case and should be larger when the size of the nano-particle becomes larger. Therefore, detailed absorption data of different sizes of nano-particle are necessary to assess this situation, but it is certain that one cannot increase the nano-particle size endlessly for scattering purposes.

To investigate how the scattering of nano-particles affects the emission of the remote phosphor structure, the angular-dependent relative intensity of blue and yellow light are measured, as shown in figure 8(a). The divergence angle of blue light in ZrO_2 nano-particles with the remote phosphor structure is larger than that of the conventional one, and blue light in the normal direction is reduced. These phenomena indicate that the scattering effect from ZrO_2 nano-particles strongly influences the optical path of blue light, which is responsible for the improvement of CCT deviation; on the other hand, the yellow light distribution of the conventional and ZrO_2 nano-particles remote phosphor structures are almost the same. This might be understood by the haze ratio dependence on the wavelength: the haze of the 10 mg cm^{-2} sample is around 30% for yellow photons (around 600 nm) and 35% for blue photons (around 450 nm). The higher the haze ratio means the stronger the scattering of photons. So yellow photons are scattered much less than blue ones, which might be beneficial for color mixing and cause less variation on CCT for ZrO_2 samples. The haze measurement in figure 6 also supports this idea that the diffused component at yellow wavelengths ($\sim$600 nm) is half that of the blue light. These results show that the CCT deviation is mainly associated with the divergence angle of blue light in the remote phosphor structure. Furthermore, the weight-dependent relative intensity of blue light with different weights of ZrO_2 nano-particles at 70° was measured, as shown in figure 8(b). It is found that the ZrO_2 nano-particle of 10 mg cm^{-2} has the optimized condition due to the highest intensity of blue light at large angles.

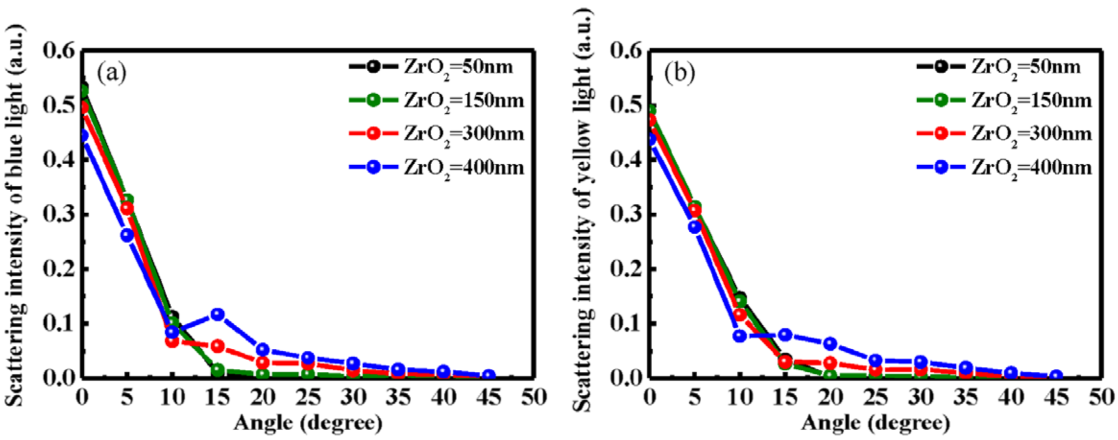

Figure 7. (a) The simulated angular-dependent scattering intensity of different ZrO_2 nano-particle sizes in blue light. (b) Same in yellow light.

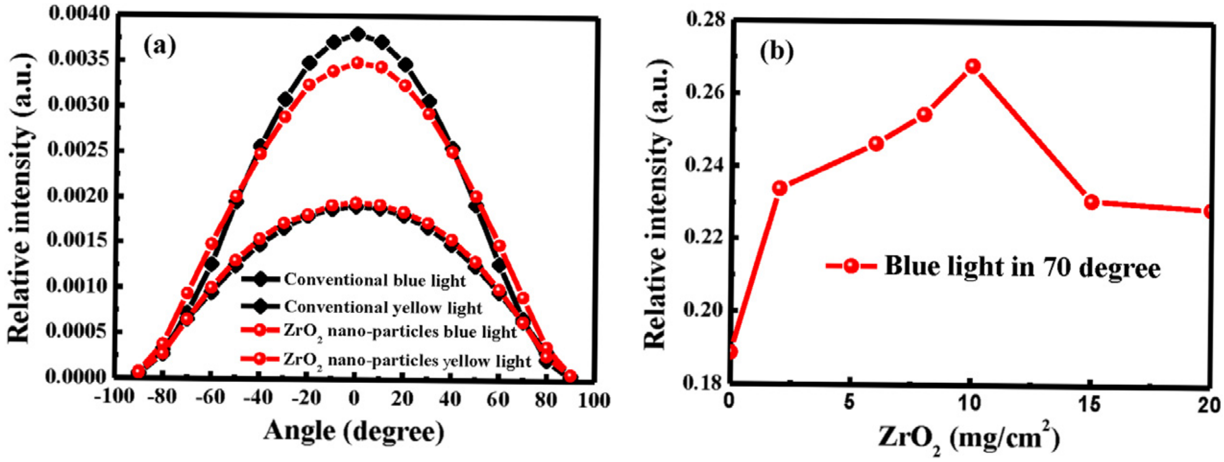

Figure 8. (a) The intensity of blue and yellow light of conventional and ZrO_2 nano-particles remote phosphor structures, (b) the relative intensity of blue light with different weights of ZrO_2nano-particles at 70°.

4. Conclusion

In this study, the superior uniformity of angular CCT in WLEDs is achieved by introducing ZrO_2 nano-particles in the remote phosphor structure. It is found that the CCT deviations could be improved by 58% using ZrO_2 nano-particles compared to the conventional remote phosphor structure. The luminous flux of the ZrO_2 nano-particles remote phosphor structure slightly increases by 2.25% at a driving current 120 mA than conventional remote phosphor structure. The scattering capability of ZrO_2 nano-particles is also demonstrated by the haze intensity. Finally, we found that the ZrO_2 nano-particles with 10 mg cm^{-2} are the optimized condition to get the lowest CCT deviations. The ZrO_2 nano-particles in the remote phosphor structure can improve the 'yellow ring' issue of the general packaged WLEDs without losing any output (in our case, the luminous flux is slightly increased). Through this package type by ZrO_2 nano-particles, we could achieve a high-quality and efficient solid-state lighting source.

Acknowledgments

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