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Enhanced reliability of LEDs encapsulated with surface-modified zirconia/silicone hybrids under thermal shock

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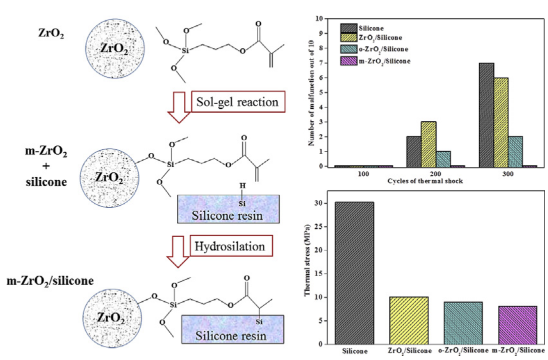
HIGHLIGHTS

- Modified zirconia (m-ZrO_2) was introduced to silicone for enhancing RI.
- The luminous flux of LEDs encapsulated with m-ZrO_2/silicone was improved by 10.1%.
- High reliability of LEDs with m-ZrO_2/silicone was observed even under thermal shock.

GRAPHICAL ABSTRACT



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ABSTRACT

This study focused on the importance of the interfacial adhesion in the zirconia (ZrO_2)/silicone hybrids as the encapsulating material on the reliability of the LEDs. Surface-modified ZrO_2 nanoparticles (m-ZrO_2) with functional groups were prepared by a sol-gel reaction which could become reactive to the silicone resin. The produced m-ZrO_2/silicone hybrid at 5 wt% had a refractive index of 1.569 at 633 nm and light transmittance of 98.9%. Moreover, the coefficient of thermal expansion was greatly reduced by the introduction of m-ZrO_2 into the silicone resin. When using this m-ZrO_2/silicone hybrid, the luminous flux of the LED was 10.1% higher than that using a neat silicone resin. Most importantly, the LEDs encapsulated with the m-ZrO_2/silicone had the best performance under thermal shock among all the LEDs tested in this study, owing to its strong interfacial adhesion between the nanoparticles and matrix. Moreover, the thermal stresses developed in hybrids were calculated and found to agree with the performance evaluation of the encapsulated LEDs under thermal shock, in which the m-ZrO_2/silicone hybrid had the lowest thermal stress. This study proposed that the m-ZrO_2/silicone hybrid material with strong

Abbreviation: m-ZrO_2, 3-methacryloxypropyl trimethoxysilane-modified zirconia; o-ZrO_2, octyl triethoxysilane-modified zirconia; AB, AB silicone resin.

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interfacial adhesion could be useful for the encapsulation of LEDs even under extreme thermal conditions.

1. Introduction

Light-emitting diodes (LEDs) have been one of the most popular light sources due to the low power consumption and long lifetime. The luminous efficiency of LEDs has experienced a substantial progress since 2000, while other conventional light sources have already reached their limits. Among the studies of LEDs, the improvement of the package material over the blue chip has attracted considerable attentions. The encapsulating material that directly attaches to blue chip can not only isolate the surface of chips from air but also enhance the light extraction efficiency by alleviating the gap of refractive index (RI) between the chip and air. According to Snell's law [1], a portion of the light emitted from the chip will be trapped by the reflection occurring on the chip-encapsulation interface [2]. Therefore, the value of RI is considered as one of the most important index while evaluating the encapsulating material. For the better extraction of light, high refractive index is necessary for encapsulating material in order to further mitigate the RI contrast [3–5].

Epoxy resins have been a competitive candidate as encapsulating material for their outstanding mechanical strength and good metal-adhesion; however, epoxies face a shortage, i.e., their long-term stability of which the yellowing occurs when they are under heat or UV exposure [6]. With high input power, LED chips encapsulated by epoxy resins are suffered from high junction temperature [7]. Thus yellowing would inevitably undermine the transparency and durability of epoxy-based materials. To solve the yellowing problem, silicone resins have been chosen as encapsulating materials; they have advantages of tunable hardness, optical transparency, and stability against exposure of UV light [8]. Nevertheless, the RI of a blue chip made from gallium nitride (=2.6) is still much higher than that of silicone resins, which can be as low as about 1.4. The introduction of metallic oxide nanoparticles is commonly adopted to boost the RI of the encapsulating material to a higher value. For example, Chen et al. [9] prepared hybrid films of trialkoxysilane-capped poly(methyl methacrylate)-titania by an *in situ* sol-gel reaction. The refractive index of the prepared hybrid films at 633 nm was increased from 1.505 to 1.867 as the TiO_2 content increased from 2.9 to 70.7 wt%. However, the abbe number was decreased from 42.8 to 12.6 due to the large particle size of TiO_2 in the hybrid material. In another study by Wang et al. [10], they demonstrated that the silicone resin doped with 0.0002 wt % TiO_2 had a higher RI value of 1.55, and yet the light extraction efficiency was increased by 4.1%. Compared to TiO_2 particles, ZrO_2 particles are less photocatalytic and therefore considered as more stable high-RI filler for encapsulation hybrids. Lei et al. [11] prepared ZrO_2/silicone hybrid materials via *in situ* sol-gel reaction of zirconium propoxide (ZPP) directly in silicone resin. The RI of the encapsulating material was increased with increasing the ZrO_2 content. The maximum luminous flux was already achieved at a value of 4.35 for the LED encapsulated with the hybrid material at 3 wt% ZrO_2, 9.6% more efficiency than that encapsulated with the neat silicone.

In the modernized world, metallic oxide particles and crystals are commonly used for the improvement of catalytic and electrochemical technology, and also to address the big challenges of energy conversion and optical storage [12,13]. Numerous works have been reported on the introduction of nanoparticles to the encapsulating materials for increasing the RI, yet the problems of the incompatibility and aggregation remain to be solved. For examples, the reliability under extreme environmental conditions and the optical transparency of the encapsulating materials still need to be examined; they are generally undermined owing to mechanical cracking and light scattering [14]. In order to achieve uniform dispersion in organic matrix without any aggregation, surface modification [15–17] of the inorganic particles is a useful and feasible approach. Hong et al. [16] grafted polystyrene onto the surface of ZnO nanoparticles to achieve stable dispersion of the particles in acetone. By introducing well-dispersed zirconia nanocrystals modified with butyric acid and 3-methacryloxypropyl trimethoxysilane (MPTMS), Chung et al. [17] were able to develop hybrid material that had good durability at a controlled temperature of 85 °C; and when applied to encapsulate the LED, it exhibited 13% more luminance intensity than a commercial encapsulating material. However, the damages of LEDs can be caused by not only the thermal aging of the encapsulating material, but also the deformation of the entire encapsulation under thermal shock. The difference between the thermal expansion coefficients of gold-wire bonding and silicone resin could generate thermal stress [18] as temperature rises and thus pull off the gold-wire bonding, leading to the failure of LEDs [19]. Moreover, the introduction of inorganic nanoparticles into organic matrix might create microvoids in the interface which would decrease the light extraction efficiency of LEDs [20]. Several approaches such as the addition of nanoparticles with low thermal expansion coefficient [21,22] have been used to reduce the thermal expansion of encapsulating materials. Furthermore, the existence of chemical bonding between the nanoparticles and matrix can enhance their compatibility and therefore restrain the thermal expansion of the nanocomposites [23,24]. It is valuable and feasible to fabricate encapsulating materials with low thermal expansion coefficient and low thermal stress by introducing compatible nanoparticles into the silicone matrix.

Previously, we directly synthesized the ZrO_2 in the silicone resin for increasing the RI value of the encapsulating material and thus the luminous flux of the LEDs [11]. Yet, we found that the thermal stability of the synthesized hybrid materials was decreased with increasing the ZrO_2 content. Moreover, the mechanical properties of the hybrid materials and reliability of such encapsulated LEDs under thermal shock remained unknown. In this study, we first proposed a simple method for the surface modification of ZrO_2 by using MPTMS having reactive vinyl groups to improve the interfacial strength and uniform distribution of the ZrO_2 nanoparticles in the silicone matrix. For comparison, an octyl triethoxysilane (OTES) without any reactive groups was also used for the modification of ZrO_2 nanoparticles. The refractive index of the resulting modified ZrO_2/silicone hybrid materials and the luminous flux of the as encapsulated LEDs were measured. Most importantly, thermal stress values of the silicone hybrids were calculated in this study and found to be correlated very well with the reliability of the encapsulated LEDs under thermal shock.