White Paper:

Pixelligent LED Encapsulation

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Introduction

Silicones have been the material of choice for Light Emitting Diode (LED) packaging due to their excellent transparency and stability at operating temperatures [1]. Silicones are not only used as encapsulants to protect LED devices, but also as the polymer matrix for phosphors to convert blue LEDs to white LEDs. With commercial silicones, LEDs have refractive index mismatches at the silicone/LED chip and silicone/phosphor interfaces. This mismatch leads to poor light transmission and/or trapped light with-in the LED device. Better light extraction can reduce internal heating, in turn reducing the dependence on heat transport materials and improving reliability.

The Refractive Index (RI) of commercial silicones used in LEDs varies from 1.41 to 1.54. To achieve RI greater than 1.42, commercial silicones employ a mix of methyl and phenyl groups on the silicone constituents in the formulation. The phenyl groups are more prone to degradation than methyl groups, and as a result, commercial silicones at RI greater than 1.5 have reduced light and thermal stability as compared to the silicones having a refractive index of 1.4. Advances in phenyl silicone technology have narrowed the performance gap,[2] but there still is a trade-off between thermo-optic stability and increase in RI for commercial LED silicones.[3] The highest RI for a commercial silicone encapsulant is 1.56 [4], and for a 150-200°C heat stable silicone encapsulant is ≤1.54.[5]

This whitepaper will highlight recent advances made at Pixelligent regarding the use of zirconia (ZrO_2) nanocrystals to raise the RI of silicones used for LED encapsulation. Pixelligent can synthesize monodispere 5nm ZrO_2 nanocrystals, and has recently scaled capacity to 6 metric tons/year. The overall keys to success in this application are:

- The ability to tailor the surface chemistry of the nanoparticles to achieve excellent dispersion with a wide variety of commercial silicones
- Thermal stability and optical transparency of cured silicone nanocomposite
- The ability to modify mechanical properties of silicone nanocomposites to meet stringent reliability and manufacturing requirements
- Product scaling for reliable supply and market relevant costs

This paper will review our recent results regarding the dispersion of ZrO_2 nanocrystals in commercial silicones, the resulting increases in RI, optical clarity, and thermal stability. Additional results will be covered in subsequent white papers.

Raising Silicone Refractive Index

Pixelligent has developed proprietary nanocrystal synthesis and capping methodologies which allow for the highest quality dispersion in silicones resulting in increased RI. As a result the tailored ZrO_2 nanocrystals can be readily incorporated into commercial silicones at high loadings to provide homogeneous agglomeration-free distribution in the cured silicone. The following examples demonstrate the RI increases that can be achieved using Pixelligent's ZrO_2 nanocrystals:

- Starting from a base silicone RI of 1.42 @ 450nm, the RI for a commercial dimethyl silicone was increased to a value of 1.58 @ 450nm by adding 80 weight percent ZrO_2. The increase of +0.15 represents an 11% increase in the RI of the dimethyl silicone.
- Starting from a base silicone RI of 1.53 @ 450 nm, the RI for a commercial methyl-phenyl silicone was increased to a value of 1.61 @ 450 nm with 80 weight percent ZrO_2. The increase of +0.08 represents a 5% increase in the RI of the methyl-phenyl silicone.

The RI versus wavelength curves for 60, 70 and 80 weight percent loading of capped ZrO_2 nanocrystals in the dimethyl and methyl-phenyl silicones are shown in Figure 1. The experimental RI results for cured silicones are in agreement with the estimated RI values based on volume loading of capped ZrO_2 nanocrystals. [6, 7]

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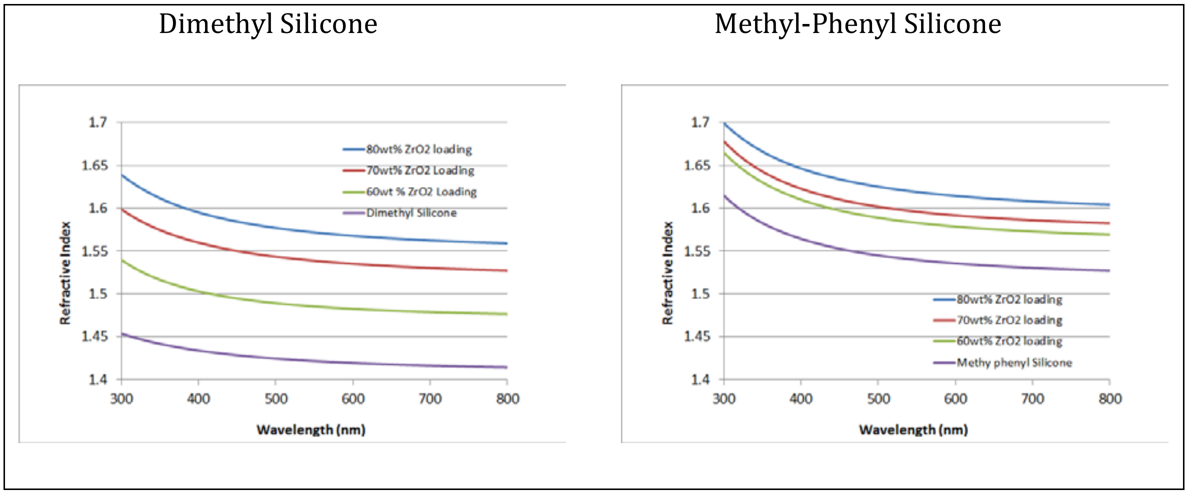

Figure 1. Wavelength dependent refractive index of cured films made with 60, 70 and 80 wt% loading of ZrO_2 in dimethyl silicone and in methyl-phenyl silicone

With incorporation of ZrO_2 nanoparticles the RI of dimethyl silicones can be increased to the same value as the methyl-phenyl silicones. The wavelength dependent RI curves for dimethyl silicone with 70 weight percent of ZrO_2 and pure methyl-phenyl silicone are shown in Figure 2. The figure clearly shows the similarity of the curves which overlap almost exactly in the 450 – 800 nm region. The two samples have a slightly different Abbe numbers, 41 for the dimethyl silicone with 70 weight percent ZrO_2 and 37 for the methyl-phenyl silicone. It is therefore possible through the use of Pixelligent's ZrO_2 nanocrystals to achieve the lumen efficiency gains of high RI methyl-phenyl silicones while maintaining the reliability of dimethyl silicone.

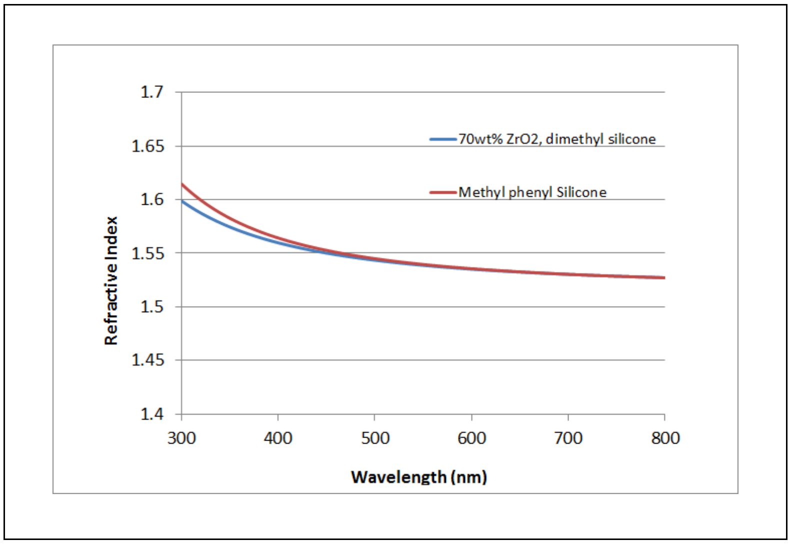

Figure 2. Wavelength dependent refractive index of cured films made with 70 weight percent ZrO_2 in dimethyl silicone as compared to methyl-phenyl silicone

Optical Clarity

Pixelligent has evaluated the clarity of cured silicones with 60, 70 and 80 weight percent loadings of ZrO_2 nanocrystals using both a spectrophotometer in transmission mode and visual inspection. Changes in optical clarity have been evaluated on initial samples, after solder re-flow, and with thermal aging between 150°C to 200°C temperature range for up to 504 hours (3 weeks). The cured silicone nanocomposites films show good transparency and clarity in samples with thickness in the range of 100µm to 2mm. The percent transmittance values for cured methyl-phenyl silicone samples with 60, 70 and 80 weight percent ZrO_2 nanocrystals are reported in Table 1. Optical images for the cured methyl-phenyl silicone with 70 weight percent ZrO_2 nanocrystal are shown in Figure 3 both after solder reflow as well as after thermal aging at 180°C for 168 hours.

Table 1. Percent transmittance values for cured methyl-phenyl silicone films with 60, 70 and 80 weight percent ZrO_2 at thickness of ≈200 μm on a glass substrate

Sample Name	**%T @ 400 nm**	**%T @ 450 nm**	**%T @ 650 nm**
Methyl phenyl Silicone	89.3	90.0	93.9
60wt% ZrO_2 loading	87.0	91.5	96.8
70wt% ZrO_2 loading	89.2	92.6	97.1
80wt% ZrO_2 loading	89.8	91.0	93.0

The higher RI cured silicone nanocomposite samples have similar transmittance values as the base silicone (Table 1). The percent transmittance values are greater than 85% in all samples. The transmission spectrum of cured silicones are wavelength independent in the 600 to 800 nm wavelength region. The loss of transparency due to scattering has been effectively suppressed by agglomeration-free dispersion of the ZrO_2 nanocrystals in the cured silicone. Solder reflow and thermal stability tests at 180°C for 168h (1 week) on ≈200 micron thick film confirmed non-yellowing behavior as compared to the base silicone material and visual inspection of cured films showed no cracking (Figure 3). Similar performance has been achieved with commercial dimethyl silicones. The ZrO_2-silicones nanocomposites are suitable in LED devices as an encapsulant and phosphor down-conversion materials.

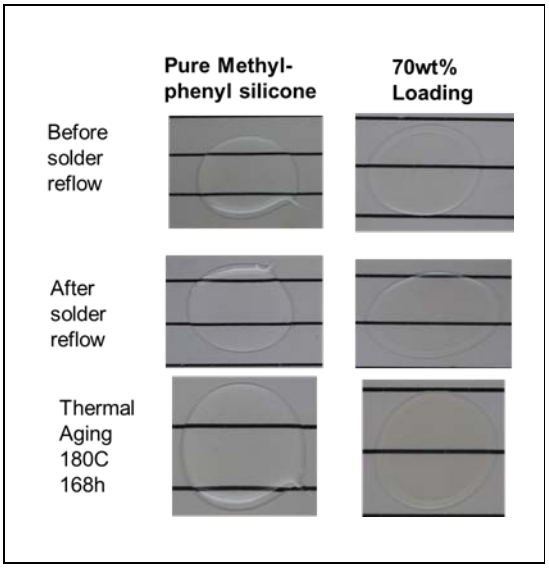

Figure 3. Images of clear ≈200 μm thick drop-cast films on glass substrate for methyl-phenyl silicone and methyl-phenyl silicone with 70 weight percent ZrO_2. Films showed no change in visual appearance and were free of cracks after solder reflow and thermal aging at 180C for 168 hours

The use of nanocrystal additives in commercial silicones requires a robust process for blending and reacting ZrO_2 nanoparticles at high loadings. Pixelligent has developed processes to reproducibly form clear films at multiple ZrO_2 nanocrystal loadings. These processes are compatible with ordinary platinum catalyzed thermal cure systems. Processes incorporating ZrO_2 nanocrystals at 60-80 weight percent loading are designed within the cure schedules specified by commercial silicone suppliers.

Conclusions

Zirconia nanocrystals made with Pixelligent's proprietary synthesis and dispersion technology can be incorporated into commercial LED silicones to significantly raise their RI. The refractive index values in commercial silicones can be increased by 5-11 % with the incorporation of ZrO_2 nanoparticles at high loading. Pixelligent's zirconia nanocrystals are compatible with silicone thermal cure process. The resulting high RI silicone nanocomposites have the potential to improve LED device performance and reliability.

References

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