



Thiol-ene photo-curable hybrid silicone resin for encapsulation of LED: enhancement of light extraction efficiency by the facile self-keeping hemisphere coating

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**Thiol-ene photo-curable hybrid silicone resin for encapsulation of
LED: enhancement of light extraction efficiency by the facile
self-keeping hemisphere coating**

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Abstract

Encapsulation with polymer materials can not only protect LED chips, but also enhance the light extraction efficiency (LEE), and thus become necessary for the fabrication of LED device. We here developed a new concept of encapsulation of LED with the photo-curable hybrid silicone resin, which can realize the facile encapsulation at room temperature. The photo-curable silicone liquid resin based on the thiol-ene photopolymerization is comprised of styrene modified mercaptopropyl-polysilsesquioxanes (St-POSS-SH) and a ladder-like polysilsesquioxane with acrylic and phenethyl sulfide groups (LPSQ). Even under the condition of open air, the obtained silicone liquid resin can be photo-cured in 2 minutes at room temperature, and can keep the shape of hemisphere during the encapsulation without the help of mold. The optical, mechanical and thermal properties of the resulted cured silicone resin were evaluated in detail. The obtained cured silicone resin is transparent, and possesses the high refractive index of 1.545(@450nm). The encapsulation of blue GaN LED with this self-kept hemisphere-shaped photo-cured silicone resin achieved the LEE enhancement of 25.6%, compared to the flat encapsulation induced by heat. On the contrast to the thermal-encapsulation, the encapsulation of LED chip with the photo-curable silicone resin do not involve in the processes of mold and demold,

which can simplify the encapsulation procedure of LED chip and decrease the operation cost obviously. We believe that this novel photo-curable silicone resin based on thiol-ene photopolymerization will be very potential for the encapsulation of LED chip.

Keywords: Encapsulation, LED chip, Photo-curable silicone resin, Thiol-ene photopolymerization

1. Introduction

GaN-based light-emitting diodes (LEDs) are an attractive light source for illumination or signs in display because of their long lifetime and high efficiency compared to those of conventional light sources [1,2]. Although the high efficiency of the LEDs can be obtained by the continuing improvement of internal quantum efficiency, the occurrence of trapped light inside a high-refractive-index semiconductor remains one of the fundamental challenge. As a result of the total internal reflection (TIR), the light-extraction efficiency (LEE) of LED is severely reduced [3-7]. As for the commercial flip GaN/InGaN-based LEDs usually built on the sapphire substrate, for example, the bare uncoated sapphire surface exhibit a high refractive index of 1.76 to air 1.0, which means that much light will be reflected back into the sapphire at the sapphire/air interface according to the Snell's law. Taking the planar uncoated bottom-emitting LED chip as an example, the light emitting only in the cone shape referred as the light-escape cone can escape outside to air (Figure 1a). The light cone [4] is defined as the boundary surrounded by the total refractive, and the maximum angle of incidence is referred to as the critical angle (θ_c).

To overcome this challenge of TIR, the LED chips are usually encapsulated in the transparent polymer materials so that not only θ_c can be increased, but also the chips can be well protected (Figure 1b). The introduction of encapsulant to LED chip causes two interfaces: sapphire substrate/encapsulant, encapsulant/air. The reflection loss at the sapphire substrate/encapsulant interface can be decreased obviously by the high refractive index of polymer encapsulant [6]. Fresnel reflection loss at the encapsulant/air interface can be reduced by the hemisphere shape of encapsulant

(Figure 1c) [6]. In the practical encapsulation of LED in industry, therefore, the commercial thermal-cured silicone resin is shaped into the hemisphere in the help of the mold to reduce Fresnel reflection loss at the encapsulant/air interface. Due to the low viscosity and good mobility at the high temperature for the thermal-curing resin (usually around 150 °C for one hour), the encapsulation shape of silicone resin is often flat and can not take shape of hemisphere without the help of the mold (Figure 1d). Therefore, two steps of mold and demold are necessary in the present thermal-encapsulation of LED chip in industry. Quite a few steps in the encapsulation process with the thermal-cured silicone resin including mold and demold, however, reduce the efficiency of encapsulation and increase the operation cost.

Instead of the thermal-cured resin, we here present a new concept for encapsulation of LED with the photo-cured silicone resin for the facile encapsulation of LED (Figure 1d). The photo-polymerization is much faster and can be carried out at the lower temperature compared to the thermal-polymerization [8]. The viscous silicone liquid resin can self-form drop of the hemisphere shape on the limited sapphire substrate due to the surface tension at the low temperature [9]. Upon the irradiation of UV-light at room temperature (RM), the liquid silicone resin is cross-linked to the polymer network, which can keep the initial hemisphere shape without the help of mold. Thus, we call the photo-cured encapsulation as the self-keeping hemisphere coating. The encapsulation procedure with the photo-cured resin does not involve processes of mold and demold compared to the thermal-encapsulation, which can simply the encapsulation procedure of LED chip and decrease the operation cost obviously (Figure 1d). Besides this significant advantage, the RM-encapsulation of LED with the photo-cured resin can make LED chip avoid the risk caused by the high temperature in the thermal-encapsulation. The chemical structures of photo-cured silicone resin for encapsulation of LED chip are shown in Figure 1e. After dropped on the naked LED chip, the liquid silicone resin with hemisphere shape can be photo-cured in 2 minutes at room temperature. It is shown that GaN LED with this hemispherical encapsulant can achieve a LEE enhancement of 25.6% compared to the LED chip with flat coating due to a reduced

Fresnel reflection loss at the encapsulant/air interface.

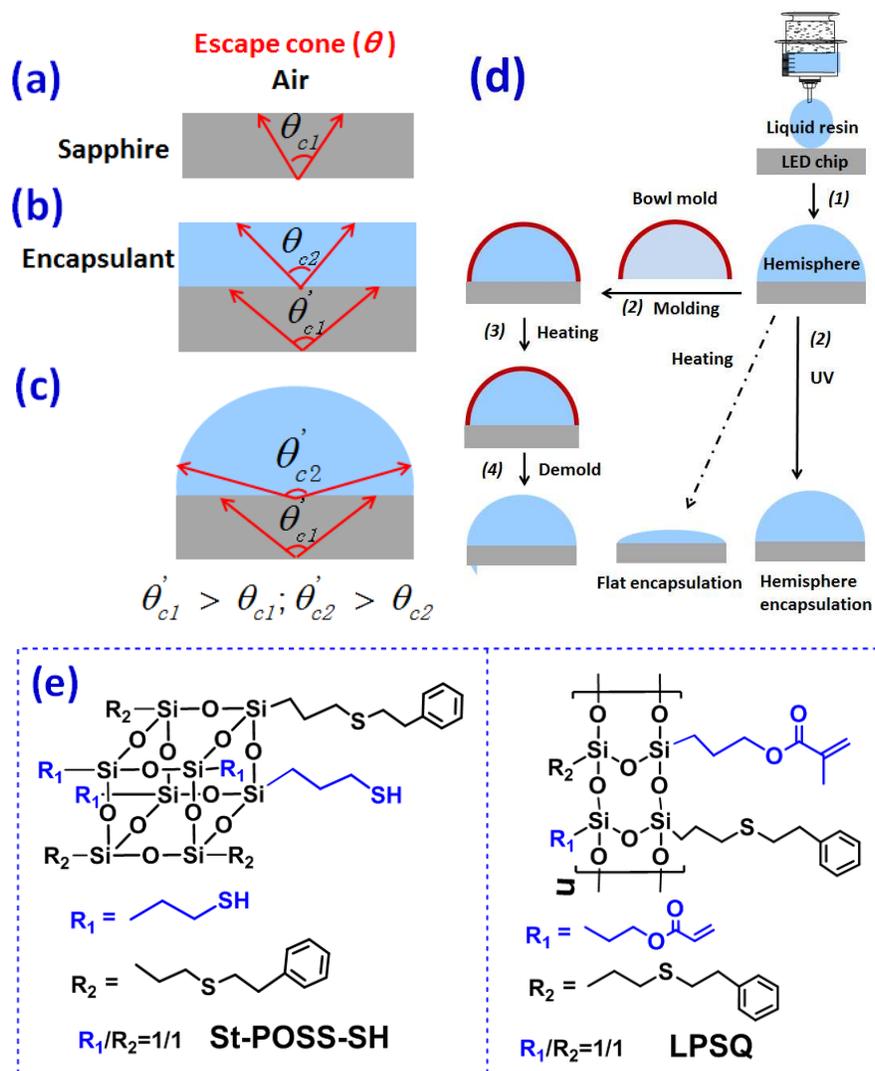


Figure 1. Schematic diagrams for the encapsulation to enhance LEE of LED chip (a-c): the light escape cone of the bare LED chip from the sapphire to air increases after encapsulation. The light loss at the encapsulant/air interface can be reduced obviously by the hemisphere-shaped encapsulant. (d) Comparison of the thermal and photo encapsulation of LED chip: the commercial thermal-encapsulation takes four steps involving in the processes of mold and demold to lead to the hemisphere-shaped encapsulant, while there are only two steps in the encapsulation of LED chip with photo-curable resin at room temperature; (e) The chemical structure of the components of the photo-curable silicone resin.

2. Results and discussion

2.1 Design and cross-linking kinetics of thiol-ene photo-curable silicone resin

In designing the chemistry and materials to encapsulate LED chips, a number of physical and chemical features were considered. The silicone hybrid resins is one of the considerable materials for the encapsulation of LED chips due to its high optical transparency, chemical and physiological stability, fracture resistance and minimal moisture absorption [10-12]. Therefore, the thermal-curable silicone is widely used for the LED encapsulant of the high performance, which usually is comprised of two components and cured at high temperature in the presence of chloroplatinic acid (HPtClO_4) as catalyst [13]. As shown in Figure 1e, our photo-cured resin is also based on the silicone, and comprised of styrene modified mercaptopropyl-polysilsesquioxanes (St-POSS-SH) and a ladder like polysilsesquioxane with acrylic and phenethyl sulfide groups (LPSQ). The detail synthesis and structural characterization of St-POSS-SH and LPSQ can be found in Supporting Information (Figures S1-S6). POSS is regard as a kind of organic-inorganic hybrid materials at a molecular level, and the incorporation of POSS can lead to the excellent mechanical and thermal properties to the resulted materials [14-17]. The ladder-like polysilsesquioxanes can be used as matrix itself, and might surpass the performance of linear polysilsesquioxanes in some properties such as thermal stability [18,19]. St-POSS-SH and LPSQ are regard as silicone cross-linkers and silicone monomers, respectively. The introduction of the phenethyl sulfide groups not only can increase the compatibility between St-POSS-SH and LPSQ, but can also increase the refractive index of the hybrid silicone materials [20]. Upon irradiation of UV-light at room temperature, our silicone resin is photo-cured through the thiol-ene polymerization, instead of the conventional radical photopolymerization. Besides the significant advantage of the less oxygen inhibition over the conventional radical polymerization, thiol-ene polymerization leads to fast curing, low shrinkage and stress, and homogeneous mechanical properties [20-26]. Furthermore, the induction of sulfur atom can increase the refractive index of the resulted encapsulant [20, 27], which is favorable for the light extraction.

To find the optimal formulation for the encapsulant of LED chip, we prepared a series of liquid mixtures with different ratio between St-POSS-SH and LPSQ, and investigated their performance systematically, as summarized in Table 1. The as-prepared mixtures of St-POSS-SH/LPSQ with different ratio are transparent liquid, which means the excellent compatibility between St-POSS-SH and LPSQ. The compatibility between two components St-POSS-SH and LPSQ is an important factor to the performance of the resulted cross-linked materials, especially for the optical transparency. The same phenyl side groups and hybrid polysilsesquioxane backbone in both St-POSS-SH and LPSQ might lead to the good compatibility.

Table 1. The formulation and physical properties of the photo-cured hybrid silicone resin. All samples were irradiated by 365 nm UV light with the intensity of 40 mW/cm² for 300s at room temperature.

St-POSS-SH/LPSQ (mol/mol)	Shrinkage (%)	Young's modulus (GPa)	Hardness (MPa)	T _d ^a (°C)	T _g (°C)	RI (450 nm)	T% ^b (450 nm)
1/1	2.1	0.16	27	325	-22	1.549	93
1/1.5	3.1	0.21	29	330	-27	1.535	93
1/2	3.5	0.30	35	336	-32	1.532	93
1/4	4.2	0.50	50	338	-36	1.529	93
0/1	5.1	0.59	65	340	-39	1.525	94

a: The temperature at the 5% loss weight of the resin networks.

b: The thickness of film is around 800 μm

The curing-reaction kinetic of liquid resin is an important parameter to the encapsulation procedure of LED chip. We first used real time FT-IR to study the photopolymerization kinetic of St-POSS-SH/LPSQ resin containing the trace amount of photoinitiator. The change of peaks at 1630 cm⁻¹ corresponding to ene (C=C) and 2555 cm⁻¹ corresponding to thiol (-SH) was monitored by FT-IR, respectively (Figure 2a and 2b). Upon irradiation of 365 nm UV-light with intensity of 40 mW/cm², all mixtures of liquid resin were photo-cured at room temperature and in the open air. The photo-curing reaction of all formulation is fast, and the balanced conversion of the C=C was achieved in the first 100 seconds (Figure 2a). Especially for

St-POSS-SH/LPSQ with thiol/ene=1/1, the conversion of C=C is higher than 92% after 60s irradiation. The final conversion of -SH for all formulation is as high as 90%, while the final conversion of C=C decreased from 92% to 40% with the decreasing ratio of thiol/ene from 1/1 to 0/1. For photo-curing of the pure LPSQ (St-POSS-SH/LPSQ-0/1), the oxygen quenching to the active radicals might lead to the low conversion of C=C due to the absence of thiol groups. These results indicated the positive effect of thiol groups on the photo-polymerization, and are consistent with the previous studies on thiol-ene photo-curing systems.

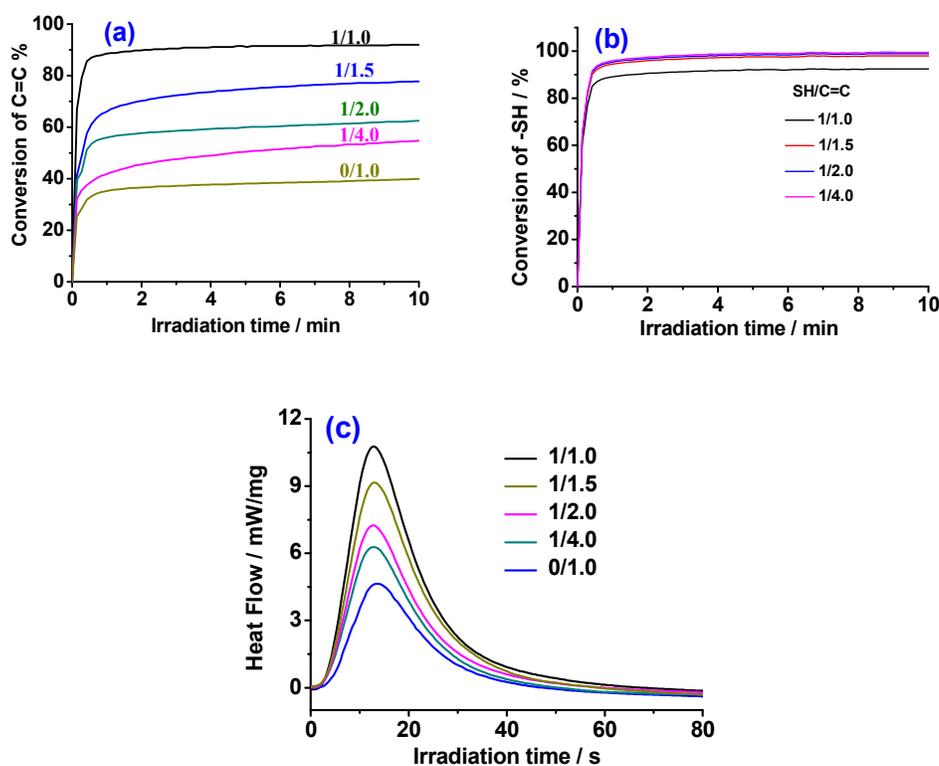


Figure 2 (a) Conversion of the C=C and (b) -SH in the polymerization of St-POSS-SH/LPSQ resins determined by real-time FT-IR. (c) Photo-DSC exotherms for the photopolymerization of St-POSS-SH/LPSQ resins. All samples were irradiated by 365 nm UV light with intensity of 40 mW/cm² at room temperature and in the open air. The content of photoinitiator is fixed at 5wt% of LPSQ.

The photo-curing kinetic of St-POSS-SH/LPSQ was also investigated by photo-differential scanning calorimetry (photo-DSC). As shown in Figure 2c, the

maximum heat flow (Hf_{max}) increased from 4.7 to 10.7 mW/mg, while time corresponding to Hf_{max} (T_{max}) decreased from 13.4 s to 12.7 s, with the increasing the ratio of thiol/ene from 0/1 to 1/1. As the main factors in the rate of photo-polymerization, both higher Hf_{max} and shorter T_{max} mean the faster photopolymerization. Thus, these photo-DSC results show that the thiol-ene photopolymerization of St-POSS-SH/LPSQ-1/1 is faster than that of the pure LPSQ. According to the amount of heat liberated, the conversion of C=C double bond increased from 41% to 93% with the addition of St-POSS-SH, which is in good agreement with the FT-IR results. The investigation of photo-curing kinetics indicated that our St-POSS-SH/LPSQ resin can be cured fast by exposure of UV-light even in the air, which makes the encapsulation of LED chip very feasible and convenient. To further understand the inhibition of oxygen in the air, we investigated the photopolymerization of our silicone resin in the air and nitrogen gas, respectively (Figure 3). The photo-curing behavior of St-POSS-SH/LPSQ-1/1 under these two conditions was almost the same, and the conversion of C=C higher than 90% can be achieved after UV-exposure of 60s, confirming that the oxygen-inhibition is negligible in the photo-curing of St-POSS-SH/LPSQ-1/1. This should be ascribed to the inherent advantage of thiol-ene photopolymerization: thiol groups can weaken the quenching effect of oxygen on the active radicals generated in the system [28]. On the contrast, the final conversion of C=C and maximum heat flow in the photopolymerization of the pure LPSQ increased significantly under the nitrogen gas, suggesting the obvious oxygen-inhibition in the conventional radical polymerization. Another major feature of our St-POSS-SH/LPSQ resin is its reduced volumetric shrinkage. After photo-cured, the volume shrinkage of film decreased with the increasing content of St-POSS-SH. The volume shrinkage of St-POSS-SH/LPSQ-1/1 resin is around 2.1%, less than that of pure LPSQ (5.1%).

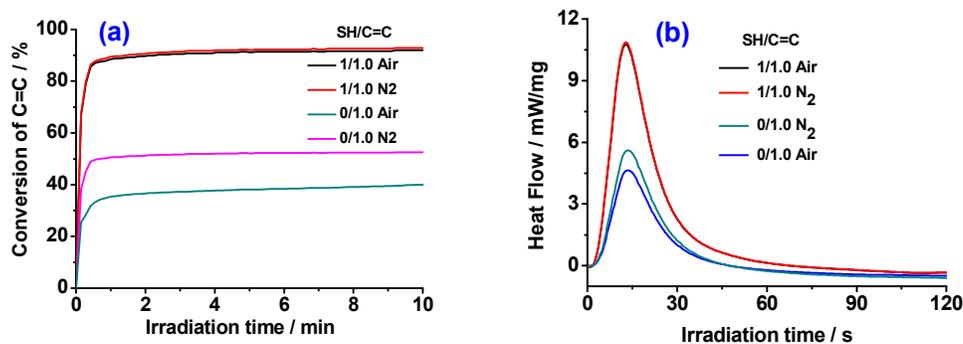


Figure 3 (a) Real time FT-IR conversion of the $-C=C-$ in the polymerization St-POSS-SH/LPSQ (1/1.0) and the pure LPSQ resin under air and N_2 environment, respectively. The content of photoinitiator is fixed at 5 wt % of LPSQ resin, and the light intensity was ca 40 mW/cm^2 . (b) Photo-DSC exotherms of photopolymerization of St-POSS-SH/LPSQ (1/1.0) and pure LPSQ resins under air and N_2 environment, respectively. The content of photoinitiator is fixed at 5 wt % of LPSQ resin, and the light intensity was 40 mW/cm^2 .

2.2 Optical, thermal and mechanical properties

We then studied the performance of the photo-cured St-POSS-SH/LPSQ films as encapsulant of LED chip including the optical, mechanical and thermal properties. As shown in Figure 4a, all of St-POSS-SH/LPSQ films are homogeneous, colorless and transparent, suggesting no phase-separation on the scale greater than the wavelength of visible light. This might be ascribed to the good compatibility between St-POSS-SH and LPSQ. The light transmittance of films with thickness of 800 μm is as high as 93% at the whole range of visible light (380-800nm). The refractive index (RI) for all films is higher than 1.515 for the whole visible range, which might be due to the introduction of phenyl ring and sulfur atom. RI of the resulted film increased with the increasing content of St-POSS-SH, and St-POSS-SH/LPSQ-1/1 film exhibited the highest RI of 1.545 at 450 nm. The enhancement of RI by St-POSS-SH might be ascribed to the introduction of sulfur atom due to the well-known heavy atom effect [27]. As RI of the substrate for LED chip is usually much higher than that of polymer encapsulant (for example, RI of sapphire is 1.760 [29]), the higher RI of encapsulant can decrease the reflect loss at the substrate/encapsulant interface.

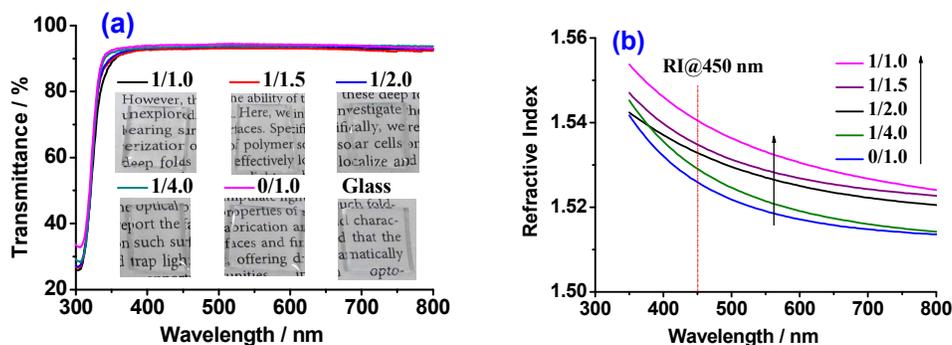


Figure 4 Transmittance curves (a) and refractive index curves (b) of the UV cured St-POSS-SH/LPSQ film. The thickness of film is around 800 μm .

Thermogravimetric analysis (TGA) and DSC (Table 1 and Figure 5) were carried out to obtain information regarding the thermal stability of the photo-cured St-POSS-SH/LPSQ film. All of these films possessed the initial decomposition temperature (T_d) higher than 320 $^{\circ}\text{C}$. The glass transition temperature (T_g) increased with the increasing content of St-POSS-SH. The enhancement of T_g by the introduction of St-POSS-SH can be explained by the POSS characteristic of inorganic nanoparticle. The Young's modulus and hardness of the cured film determined by nanoindentation test decreased with the increasing content of St-POSS-SH. Young's modulus and hardness of the St-POSS-SH/LPSQ-1/1 film without any reinforcing agent are still 160 Mpa and 27 MPa, respectively, which are much higher than that of the PDMS (0.2-1.8 MPa) [30, 31]. Based on these results including the photo-curing kinetics, optical, thermal and mechanical performance, St-POSS-SH/LPSQ-1/1 resin was chosen as the encapsulant of LED chip in the following device studies.

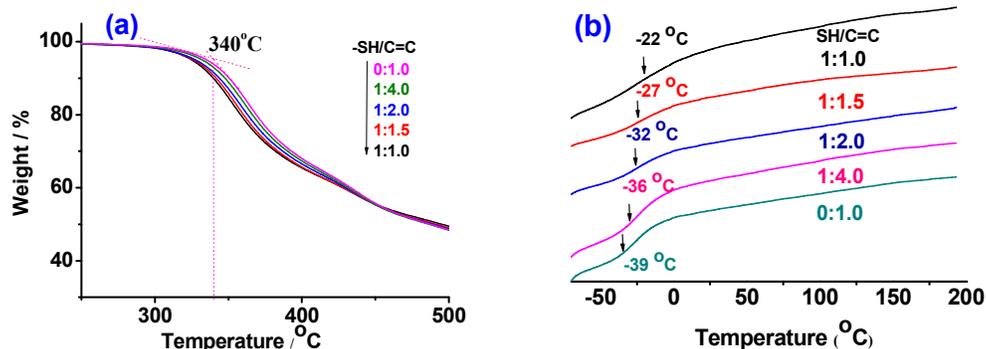


Figure 5. TGA (a) and DSC (b) curves of cured St-POSS-SH/LPSQ film with the mole ratio of thiol/ene at 1/1.0, 1/1.5, 1/2.0, 1/4.0 and 0/1.0, respectively.

2.3 Encapsulation of LED chip

To demonstrate the feasibility of our photo-cured silicone resin in encapsulation of LED chip, flip blue GaN LED chip ($\lambda=450$ nm, 3×3 mm) with the sapphire substrate was drop coated by a fixed volume of St-POSS-SH/LPSQ-1/1 liquid resin (Figure 1d and Figure 6a). The surface tension of the viscous liquid silicone resulted in the hemisphere shape of liquid drop on the limited LED chips surface. Upon the direct irradiation of 365 nm UV-light for 5 minutes at room temperature, the liquid drop became completely solid with the hemispherical shape on the sapphire substrate (Figure 6a, inset). The hemispherical package is difficult to be detached from the LED chip, indicating the adhesion of the silicone resin to LED chip is good. This might be ascribed to the presence of sulfur atom, which can enhance the adhesion of silicon resin to the inorganic substrate. For comparison, the coated LED chip was also thermal-cured at the commercial condition (150 °C for 60 min), the coating on the sapphire substrate became almost flat because the liquid drop flowed out of the limited surface at the high temperature. The similar behavior of the thermal induced flat encapsulation happened to the commercial thermal-curable silicone resin (eg. Dowcorning 6550) too. For easy comparison and analysis, we defined θ_e as the encapsulated angle, which is the contact angle of the liquid resin drop on the sapphire substrate (Figure 6a, inset). The electroluminescence spectra at a DC 350 mA current injection and light output power of LED chip with both hemispherical and flat encapsulation were measured, as well as the naked LED chip (unencapsulated) as reference. As shown in Figures 6a and 6b, LEE and light output power of LED chip increased after encapsulation with silicone resin. The LED chips with the flat and hemispherical encapsulation exhibited 4.3% (5.6% for Dowcorning 6550 flat encapsulation, showing in Figure S7) and 26.3% higher LEE than that of the naked LED chip. The obvious enhancement of LEE by the hemispherical encapsulant can be explained by the reduced Fresnel reflection loss at the curved encapsulant/air

interface.

The effect of the encapsulant shape on the light output power of LED chips was evaluated. The encapsulation angle was controlled by the amount of liquid resins dropped on the limited sapphire surface. As shown in Figure 6c, LEE of the encapsulated LED chips increased with the increasing encapsulation angle. The enhancement of LEE by the encapsulant angle can be explained by the analysis of the model shown in Figure 6a. The escape light cone at encapsulant/air interface can be enhanced by the increasing encapsulation angle, resulting in the reduced Fresnel reflection loss. When the encapsulant angle is 90 °C, for example, all of light from the center area is perpendicular to the encapsulant/air interface, and can escape outside. If the encapsulant shape is hyper-hemisphere (θ_e), more light from the other area can emit outside and the encapsulated LED chip can achieved the enhancement of 30.7%.

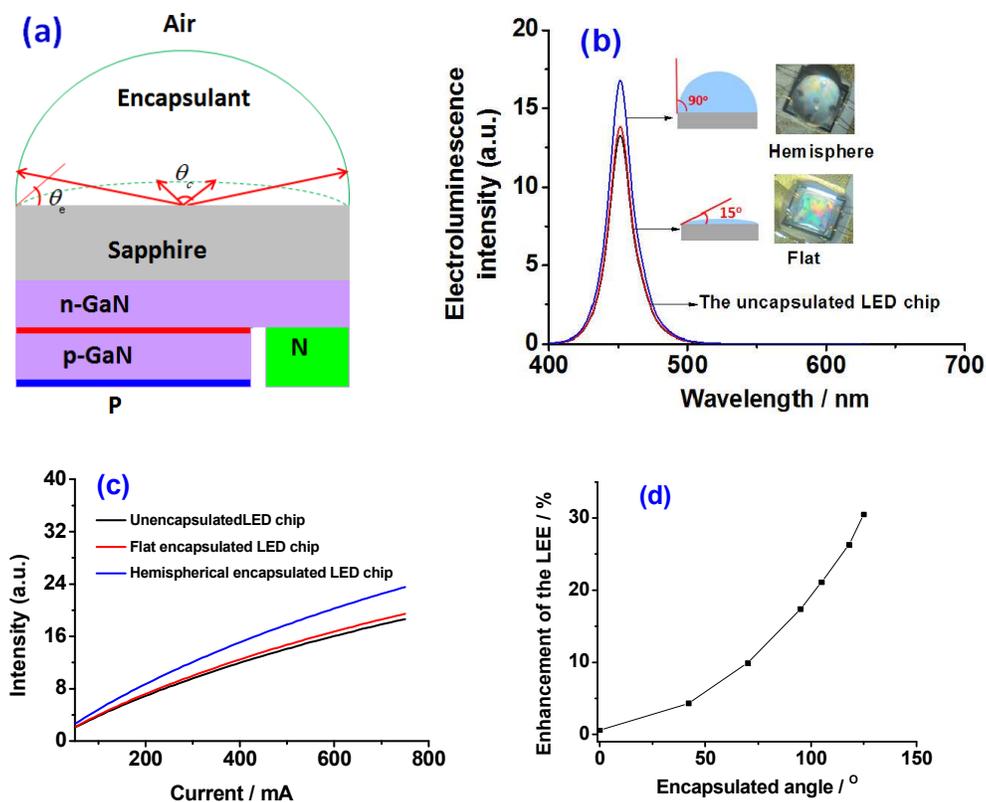


Figure 6 (a): The flip GaN LED chip and its encapsulant with different encapsulated angle (θ_e); The electroluminescence spectra (b) and light output power versus forward drive current (c) of the flat and hemispherical encapsulated LED chips as well as the uncapsulated LED chip. LED chip

used for evaluation is the blue GaN LED chip ($\lambda=450$ nm, 3×3 mm); (d) Light extraction efficiency enhancement as a function of the encapsulated angle.

To further understand the advantages of our photo-curable resin, we also encapsulated the blue LED chip with hemisphere-shaped thermal-encapsulation by using commercial thermal-curable silicone resin (Dowcorning 6550) and polycarbonate bowl as the encapsulant and shape mold, respectively. As shown in Figure S7, the LEE enhancement of the hemispherical encapsulated LED chip with polycarbonate mold is around 25%, which is closed to our self-keeping hemispherical encapsulation by photo-curable silicone resins.

3. Conclusion

We demonstrated a proof of new concept that the photo-curable silicone resin based on thiol-ene photopolymerization can realize the facile encapsulation of LED chip at room temperature. The liquid silicone resin can be photo-cured in 2 mins under the condition of open air at room temperature, and the resulted cured silicone possesses the good optical, thermal and mechanical properties. Because of the fast photo-curing at room temperature, this photo-cured liquid silicone resin can keep the shape of hemisphere during the encapsulation without the help of mold. The encapsulation of blue GaN LED with the self-kept hemisphere-shaped photo-cured silicone achieved the LEE enhancement of 25.6%, compared to the flat encapsulation induced by heat. On the contrast to the thermal-encapsulation, the encapsulation of LED chip with the photo-curable silicone does not involve in the processes of mold and demold, which can simply the encapsulation procedure of LED chip and decrease the operation cost obviously. This novel photo-curable silicone will be very potential for the facile encapsulation of LED chip.

4. Acknowledgments

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5. Experimental Section

Measurement and characterization: ^1H NMR and ^{29}Si NMR spectra were recorded on a Varian Mercury Plus-400 NMR spectrometer (400 MHz) with CDCl_3 as the deuterated solvent. FTIR spectra were recorded on a Perkin-Elmer Paragon 1000 FTIR spectrometer. Conversions were calculated from the ratio of peak area to the peak area prior to polymerization. Photopolymerization kinetic was carried out on the photo-DSC measurements (DSC 6200 Seiko Instrument) with a high-pressure mercury lamp as light source. TGA was performed in nitrogen with a Perkin-Elmer TGA 2050 instrument at a heating rate of $10^\circ\text{C}\cdot\text{min}^{-1}$. For each measurement, the samples were maintained at 100°C under vacuum for 12 h to remove any solvent from the sample before measurement. The viscosities of hybrid resists were determined at 25°C using a NDJ-79 rotational viscometer. Measurements were acquired on 10-15 mL samples at a rotation speed of 5-75 rpm. The Young's modulus of the cured film was measured at room temperature with a commercial nanoindentation system (Hysitron TI-900 TriboIndenter, USA). According to ISO 3521, a pycnometer was used to measure the density (ρ) of uncured and cured resist specimens. The volumetric shrinkage was calculated using the formula:

$$\Delta V\% = \left(1 - \frac{\rho_{\text{uncured}}}{\rho_{\text{cured}}}\right) \times 100\%.$$

Encapsulation and measurement of LED chip: St-POSS-SH/LPSQ-1/1 resins with 5 wt % I907 were filled into injection syringe, fixed volume drops was controlled by procedure and adhere to the LED chips' limited surface, then the LED chips with St-POSS-SH/LPSQ-1/1 resins was exposed under UV-365nm light for 5 minutes to obtain the self-keeping half spherical encapsulation. The encapsulated angle was changed by changing the volume of the resins drop. The measurements of electroluminescence spectra and light output power were carried out in an integrating sphere system (HAAS-2000) assembled with fiber spectrometer.

The synthesis and characterization of St-POSS-SH and LPSQ can be found in Supporting Information

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Table of content

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