High-refractive-index TiO$_2$-nanoparticle-loaded encapsulants for light-emitting diodes

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A high-refractive-index (high-$n$) encapsulant is highly desirable because it can result in enhancement of light-extraction efficiency from high-$n$ semiconductor light-emitting diode (LED) chips. A uniform dispersion of TiO$_2$ nanoparticles in epoxy for LED encapsulation is demonstrated for surfactant-coated TiO$_2$ nanoparticles by drying, mixing with a solvent, refluxing, centrifuging, and mixing with epoxy. The refractive index of surfactant-coated TiO$_2$-nanoparticle-loaded epoxy is 1.67 at 500 nm, significantly higher than that of conventional epoxy ($n = 1.53$). Theoretical analysis of optical scattering in nanoparticle-loaded encapsulants reveals that the diameter of nanoparticles and the volume loading fraction of nanoparticles are of critical importance for optical scattering. Quasispecular transparency of the encapsulant film can be achieved if the thickness of the film is kept below the optical scattering length. A graded-refractive-index multilayer encapsulation structure with the thickness of each layer being less than the mean optical scattering length is proposed in order to reduce optical losses from scattering and Fresnel reflection. Furthermore, three-dimensional optical ray-tracing simulations demonstrate that encapsulants with an optimized scattering coefficient, $k_s$, benefit from optical scattering by extracting deterministic trapped modes. Theoretical light-extraction enhancements larger than 50% are found when comparing scattering-free to scattering encapsulation materials. © 2008 American Institute of Physics [DOI: 10.1063/1.2903484]

I. INTRODUCTION

One of the fundamental limitations in the light-extraction efficiency of light-emitting diodes (LEDs) is the occurrence of trapped light within high-refractive-index (high-$n$) semiconductors such as III-V phosphides, arsenides, and nitrides. Based on Snell’s law, the angle of the light-escape cone for the semiconductor-air interface is very small due to the high-refractive-index contrast. For example, the escape-cone angle for unencapsulated AlGaInP ($n_{\text{AlGaInP}} = 3.35$) is only $\sim 17^\circ$, resulting in light-extraction efficiencies of only a few percent. The light outside the escape cone is trapped inside the semiconductor and thus likely lost by eventual absorption. Although major efforts have been made to alleviate the light-escape problem, for example, by optimizing the geometrical shape of the LED die$^1$ and by surface roughening,$^2$–$^5$ the fundamental problem of the high-refractive-index contrast between semiconductor and air remains unsolved. Encapsulants such as epoxy and silicone reduce the refractive index contrast resulting in a larger light-escape cone, as shown in Fig. 1(a). However, the refractive indices of typical encapsulants are only $\sim 1.5$, far below the refractive indices of III-V nitrides and phosphides ($n \approx 2.5$–3.5). The extraction efficiency ratio for light coupled into epoxy to light coupled into air is given by$^6$

$$\eta_{\text{epoxy}} = \frac{1 - \cos \theta_{\epsilon, \text{epoxy}}}{1 - \cos \theta_{c, \text{air}}},$$

where $\theta_{\epsilon, \text{epoxy}}$ and $\theta_{c, \text{air}}$ are the critical angles for total internal reflection of the epoxy-semiconductor and air-semiconductor interface, respectively. As the refractive index of the encapsulant increases, the calculated light-extraction efficiency increases rapidly as shown in Fig. 1(b). This represents the clear motivation for developing encapsulants with higher refractive indices than typical epoxies or silicones.
High-refractive-index nanoparticles, such as titania (TiO₂, \(n_{\text{TiO}_2} = 2.7\)), that are dispersed uniformly in an encapsulant, as conceptually drawn in Fig. 2, will increase the overall refractive index of the encapsulant.

Consider the phase velocity of an optical wave traveling through a medium, given as

\[ v_{\text{ph}} = \frac{c}{n}, \]  

where \(c\) is the speed of light in vacuum and \(n\) is the refractive index of the medium. For a given distance, the wave propagation time through TiO₂ will be longer than through neat epoxy due to the higher refractive index of TiO₂. We define the total propagation time by

\[ \tau_{\text{tot}} = \tau_{\text{TiO}_2} + \tau_{\text{epoxy}}, \]

where \(\tau_{\text{TiO}_2}\) and \(\tau_{\text{epoxy}}\) are the propagation times through TiO₂ and epoxy, respectively. A TiO₂-nanoparticle-loaded epoxy medium of volume loading fraction \(L\), over a distance \(d\), has a total propagation time of

\[
\tau_{\text{tot}} = \frac{d_{\text{TiO}_2}}{v_{\text{ph,TiO}_2}} + \frac{d_{\text{epoxy}}}{v_{\text{ph,epoxy}}} = \frac{d_{\text{TiO}_2} n_{\text{TiO}_2}}{c} + \frac{d_{\text{epoxy}} n_{\text{epoxy}}}{c}
\]

\[ = \frac{V_{\text{tot}}}{A} \left( \frac{n_{\text{TiO}_2}}{c} + \frac{n_{\text{epoxy}}}{c} \right) = V_{\text{tot}} \frac{L n_{\text{TiO}_2} + (1 - L) n_{\text{epoxy}}}{A c}, \]

where \(V_{\text{tot}}\) is the total volume, \(A\) is the cross-sectional area, and we have neglected any dispersion effect. Let us denote the effective refractive index of the TiO₂-loaded epoxy as \(n_{\text{eff}}\). We then can write

\[ \tau_{\text{tot}} = \frac{V_{\text{tot}} n_{\text{eff}}}{A c}. \]

Comparison of Eqs. (4) and (5) yields an effective refractive index of

\[ n_{\text{eff}} = \frac{V_{\text{tot}} n_{\text{TiO}_2} + V_{\text{epoxy}} n_{\text{epoxy}}}{V_{\text{tot}}}, \]

where \(V_{\text{TiO}_2}\) and \(V_{\text{epoxy}}\) are the TiO₂ and epoxy volumes, respectively. The calculated refractive index of the TiO₂-epoxy composite is shown in Fig. 3 as a function of the TiO₂ volume loading fraction \(L\). Inspection of the figure reveals that the refractive index of the TiO₂-epoxy composite increases linearly with the TiO₂ volume loading fraction.

The effective medium approximation (EMA) is also shown in Fig. 3 with respect to TiO₂ volume loading fraction. Comparison of the two theoretical curves shows that they are very similar.

The volume loading fraction of TiO₂ in epoxy is related to the mass loading fraction by

\[ L = \frac{\text{Volume of TiO}_2}{\text{Volume of TiO}_2 + \text{Volume of epoxy}}, \]

\[ = \frac{M}{\rho_{\text{TiO}_2}} + \frac{1 - M}{\rho_{\text{epoxy}}}, \]

where \(M\) is the TiO₂ mass loading fraction, \(\rho_{\text{TiO}_2}\) is the mass density of TiO₂, and \(\rho_{\text{epoxy}}\) is the mass density of epoxy. The volume loading fraction has a nonlinear relationship with respect to mass loading fraction, as shown in Fig. 4, due to the density difference of the polymer and TiO₂.
If nanoparticles are in an ordered, latticelike arrangement within a medium, with the nanoparticles having a diameter much less than the wavelength of incident light, then the nanoparticles will not induce optical scattering. In a uniform distribution of nanoparticles, given by the Poisson distribution, Rayleigh scattering will occur due to refractive index fluctuations throughout the medium. Additionally, the high surface-to-volume ratios at the nanoscale often favor attractive forces between nanoparticles, which result in their agglomeration. The tendency of nanoparticles to agglomerate will result in excess optical scattering, i.e., scattering will be larger than Rayleigh scattering. Therefore, to realize high-n nanoparticles-loaded encapsulants without scattering and absorption losses, uniform dispersion and stabilization of nanoparticles are needed.

In the present work, we demonstrate an increase in refractive index of TiO2-nanoparticle-loaded epoxy by uniform dispersion of surfactant-coated TiO2 nanoparticles in epoxy. The Rayleigh scattering of TiO2-nanoparticle-loaded epoxy is highly dependent upon nanoparticle radius and volume loading fraction. A graded-refractive-index-encapsulation concept is proposed to reduce optical losses by scattering and Fresnel reflections. Furthermore, three-dimensional ray-tracing simulations are performed to investigate how optical scattering by nanoparticles influences the light-extraction efficiency. We show that scattering by nanoparticles in encapsulants can strongly improve light extraction when the scattering coefficient $k_s$ is optimized.

II. EXPERIMENT AND RESULTS

TiO2 commercial nanoparticles from Nanophase Technologies Corporation of average diameter of 40 nm have a surface area of 35 m$^2$/g, illustrating the enormous importance of surface effects. The TiO2 nanoparticles are produced by a vapor-phase method, in which electrical arc energy is applied to solid titanium to generate titanium vapors at a high temperature. Then, oxygen is added to the vapor, cooled at a controlled rate so that the titanium atoms react with oxygen and condense to form TiO2 nanoparticles. X-ray diffraction analysis of the TiO2 nanoparticles shows that the dominant crystal structure is the rutile phase. TiO2 has a refractive index of 2.7 at 500 nm. Usually, as-received TiO2 nanoparticles contain ~1 wt % of molecular water and surface hydroxyls. Figure 5(a) shows an optical micrograph of the as-received TiO2 nanoparticles. Many of the TiO2 nanoparticles stick together to form weak agglomerates possibly due to adsorbed molecular water and hydroxyls on the surface of the nanoparticles. A cleaning/drying process is carried out at 125 °C in an N$_2$ ambient-pressure glove box for 24 h to dry the nanoparticle surfaces. In an effort to prevent the reabsorption of H$_2$O and other containments after the drying step, the particles are immediately mixed in toluene and magnetically stirred. Then, appropriate amounts of surfactant A or B (Ref. 8) are mixed into the solution. The surfactants adsorb onto the nanoparticle surface and modify inter-particle forces thereby enhancing particle dispersibility. To coat the nanoparticles with the surfactants effectively, a reflux system is used for 48 h. In the refluxing process, a solution is heated near its boiling point; the vapor produced rises and condenses back to the solution after coming in contact with a water-cooled surface. The purpose of refluxing is to thoroughly mix the surfactant with the nanoparticles to produce a solution of nonagglomerated nanoparticles. The resulting solution is placed in a centrifuge for removal of toluene. The nanoparticles are subsequently washed with new toluene to remove additional contaminants and re-centrifuged. The resultant surface-modified TiO2 nanoparticles are dried at 125 °C in an N$_2$ ambient-pressure glove box for 24 h. After drying, the surface-modified TiO2 nanoparticles are mixed into epoxy via a planetary mixer. For curing preparation, a cationic photoinitiator is added into the solution. The nanoparticle loaded epoxy is spin coated on a silicon substrate and exposed to ultraviolet radiation from a xenon lamp for 90 s to complete curing. Figure 5(b) shows an optical micrograph of TiO2 nanoparticles dispersed in epoxy without surface modification, and, as a consequence, significant agglomeration of TiO2 nanoparticles is observed. Figures 5(c) and 5(d) show optical micrographs of surface-modified TiO2 nanoparticles dispersed in epoxy with surfactants A and B, respectively. Comparison of the micrographs demonstrates that the chemistry of the surfactant directly affects the dispersibility of the nanoparticles in polymeric materials. Significant agglomeration of the nanoparticles is still observed with the nanoparticles coated by surfactant A. However, when the surface of the TiO2 nanoparticles is modified by using the proper surfactant, surfactant B, particle dispersibility is drastically enhanced, as shown in Fig. 5(d).

The spectral reflectivity of TiO2-loaded epoxy and unloaded (neat) epoxy spin coated on silicon are measured, as shown in Figs. 6(a) and 6(b), respectively. The reflectivity curves contain periodic oscillations, whose simulation indi-
indicates film thicknesses of 2.33 and 2.80 μm for TiO2-loaded epoxy and unloaded epoxy, respectively. The thickness values are also measured by ellipsometry and cross-sectional scanning electron microscopy (SEM) and these measurements agree with the thicknesses of the spectral reflectivity simulations. Based on the wavelength dependent reflectivity curves, the refractive index of TiO2-loaded epoxy and unloaded epoxy is evaluated using the Cauchy model, which expresses the refractive index as

\[
n(\lambda) = A_n + \frac{B_n}{\lambda^2} + \frac{C_n}{\lambda^4},
\]

where \(A_n\), \(B_n\), and \(C_n\) are constants. Inspection of Fig. 6(c) indicates a clear increase of refractive index for the TiO2-loaded encapsulant with loading factor \(L=0.1\) (\(n = 1.67\) at \(\lambda=500\) nm) compared to unloaded epoxy (\(n = 1.53\) at \(\lambda=500\) nm). The refractive index value of the TiO2-loaded encapsulant with loading factor \(L=0.1\) follows the trend shown in Fig. 3. The overall reflectivity values of the TiO2-nanoparticle-loaded encapsulant are less compared to unloaded epoxy signifying a refractive index enhancement due to the reduction in reflectance at the Si-epoxy interface for the high-refractive-index medium (the reflectance from the epoxy-air interface is less significant at these encapsulant refractive index values).

III. DISCUSSION

A. Scattering by nanoparticles

The refractive index variation inside high-\(n\) nanoparticle-loaded encapsulants results in optical scattering by nanoparticles. If the particle size is much less that the wavelength of light (e.g., one-tenth of the wavelength), Rayleigh scattering is the dominant scattering mechanism. The Rayleigh scattering cross section of a nanoparticle inside a polymer host is given by

\[
C_{\text{scat}} = \frac{8\pi^6 n_{\text{nano}}^4}{3} \left( \frac{n_{\text{nano}}^2 - n_{\text{host}}^2}{n_{\text{nano}}^2 + 2n_{\text{host}}^2} \right)^2 \left( \frac{2r_{\text{nano}}}{\lambda s} \right)^6,
\]

where \(r_{\text{nano}}\) is the radius of the spherical nanoparticle, \(k\) is the wave number \((2\pi/\lambda)\), and \(n_{\text{nano}}\) and \(n_{\text{host}}\) are the refractive indices of the nanoparticle and polymer host, respectively. Rearranging terms in Eq. (9) yields

\[
C_{\text{scat}} = \frac{2\pi^5}{3} n_{\text{host}}^3 \left( \frac{n_{\text{nano}}^2 - n_{\text{host}}^2}{n_{\text{nano}}^2 + 2n_{\text{host}}^2} \right)^2 \frac{2(r_{\text{nano}})^6}{\lambda_0},
\]

The scattering cross section is related to the scattering coefficient \(k_s\) by

\[
k_s = NC_{\text{scat}},
\]

where \(N\) is the concentration of scattering centers (nanoparticles per unit volume), which is equal to \(L/V_{\text{nano}}\), where \(L\) is volume loading fraction. Therefore, the Rayleigh scattering coefficient of a nanoparticle-loaded polymer is

\[
k_s = \frac{2\pi^5}{3} \left( \frac{n_{\text{nano}}^2 - n_{\text{host}}^2}{n_{\text{nano}}^2 + 2n_{\text{host}}^2} \right)^2 \frac{(2r_{\text{nano}})^6}{\lambda_0^3} \frac{L}{(4/3)\pi r_{\text{nano}}^3}.
\]

The inverse of the scattering coefficient, \(1/k_s\), which is the mean distance between scattering events, is highly dependent upon nanoparticle radius and volume loading fraction. Figure 7 shows the calculated mean scattering length of TiO2-loaded epoxy with various nanoparticle radii at specified loadings assuming \(n_{\text{nano}}=2.7\), \(n_{\text{host}}=1.5\), at \(\lambda=500\) nm. For a nanoparticle of radius of 20 nm and a volume loading fraction of 0.5 in epoxy (\(n_{\text{host}}=1.5\)), the mean scattering length is \(k_s^{-1}=27\) μm. This calculation illustrates that, in this case, the specular transparency (transparency of a medium with little scattering) can be obtained only for films with thickness up to 27 μm.

B. Graded-index encapsulation

Non graded high-\(n\) nanoparticle-loaded encapsulants will produce Fresnel-reflection losses at the abrupt encapsulant-air interface. Nanoparticle-loaded encapsulants that consist of multiple encapsulant layers with gradually decreasing refractive-index values, whose layer thicknesses are less than the mean scattering length to maintain specular
or quasispercular transparency, will minimize Fresnel reflection and scattering losses while maximizing transmittance. The reflection at normal incidence can be expressed in terms of the Fresnel transmission coefficient for two media as

$$T_f = \frac{4n_1n_2}{(n_1 + n_2)^2},$$

where $n_1$ and $n_2$ are the refractive index values of media 1 and 2, respectively. For a graded encapsulant, multiple reflection and transmission events at each interface will contribute to the overall transmittance and reflectance, as shown in Fig. 8. Accounting for multiple reflections within a layer bounded by refractive index contrasts, we analytically find that the total transmittance for a graded encapsulant of $G$ layers can be expressed as

$$T_{tot} = 4 \cdot \prod_{j=2}^{G+1} \frac{n_{j-1}n_j}{(n_{j-1}+n_j)^2},$$

where $n_0$ and $n_{G+1}$ are the semiconductor and air refractive index values, respectively, and $n_1, n_2, \ldots, n_G$ represent the graded-index encapsulant layers following $n_0$.

The refractive index value of each layer should be optimized to yield maximum transmittance based on Eq. (14). We find that the optimal refractive index producing maximum transmittance for $G$ layers is given by

$$n_m = (n_0)^{m/(G+1)},$$

where $m=1,2,\ldots,G$ is the first, second, and $G$th layer placed on top of the semiconductor.

Assuming normally incident light for a graded-index encapsulant, as shown in Fig. 9(a), Eqs. (13) and (14) can be used to calculate the GaN and GaP transmittance values for encapsulant layers that are so thick that thin-film interference effects can be neglected. Figure 9(b) shows the calculated transmittance from GaN ($n=2.5$) and GaP ($n=3.45$) to air ($n=1.0$) while varying the number of optimized encapsulant layers based on Eqs. (14) and (15). Optical transmittance is significantly enhanced as the number of layers increases due to the strong reduction of Fresnel reflection.

C. Optimum scattering for light extraction

Three-dimensional ray-tracing simulations are performed in order to investigate the effect of optical scattering by nanoparticles in an encapsulant on light-extraction efficiency. A lambertian surface emitter located inside a lightly absorbing cubic encapsulant of volume (5 mm)$^3$ is shown in Fig. 10. Optically trapped modes in the encapsulant are generated from light obliquely incident at the encapsulant-air refractive-index boundary due to total internal reflection. For weak scattering, the deterministic trapped modes are unable to escape into free space and are ultimately absorbed by the encapsulant. For strongly scattering nanoparticle-loaded encapsulants, the optical scattering length, $k_s^{-1}$, is short, but the light rays’ optical path length is long. The long optical path length eventually exceeds the photon absorption length, $a^{-1}$, resulting in photon absorption by the encapsulant, thus decreasing light-extraction efficiency. The light rays that escape the cubic encapsulant are captured by a far-field receiver, which is used to assess the light-extraction efficiency value of the lambertian surface emitter. An optimized amount of scattering is beneficial, as shown in Fig. 10, which indicates that the enhancement of light-extraction efficiency is greater than 50% for an optimized scattering coefficient $k_s$. An encapsulant with an optimized $k_s$ will enhance light-extraction efficiency by optically scattering the deterministic trapped
modes of light into free space. Therefore, remote phosphor-based LEDs (Ref. 13) that contain whispering gallery modes\textsuperscript{14} will benefit greatly from an encapsulant with an optimized scattering coefficient $k_s$.

IV. CONCLUSIONS

TiO$_2$-nanoparticle-loaded encapsulants for LEDs are fabricated. As-received TiO$_2$ nanoparticles with average diameter of 40 nm are dried, mixed with a solvent, refluxed, centrifuged, and mixed with epoxy to produce surfactant-coated nanoparticles. A drastic reduction of TiO$_2$ agglomeration in epoxy is observed for surfactant-coated TiO$_2$ nanoparticles. The refractive index of the TiO$_2$-nanoparticle-loaded epoxy film is $n=1.67$ at $d=500$ nm, much higher than that of conventional unloaded epoxy, $n =1.53$ at $\lambda=500$ nm. Theoretical calculations indicate that the optical scattering in nanoparticle-loaded epoxy is highly dependent upon the radius and volume loading fraction of the dispersed nanoparticles. For the reduction of optical losses by scattering and Fresnel reflection by nanoparticle-loaded encapsulants, we propose a graded-index multilayer encapsulation with layer thicknesses less than the mean optical scattering length. In addition, ray-tracing simulations reveal that optical scattering in encapsulants does not necessarily reduce light-extraction efficiency; rather, it is shown that an enhancement greater than 50\% can occur for encapsulants with an optimized scattering coefficient.

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8The chemical compositions of surfactant A and surfactant B are trade secrets of Troy Research Corporation and cannot be publicly disclosed.


