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Citation: Appl. Phys. Lett. **102**, 143302 (2013); doi: 10.1063/1.4800941
View online: http://dx.doi.org/10.1063/1.4800941
View Table of Contents: http://apl.aip.org/resource/1/APPLAB/v102/i14
Published by the American Institute of Physics.

# Observing and modeling light propagation in polymer films

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(Received 28 December 2012; accepted 25 March 2013; published online 10 April 2013)

Light propagation within a thin luminescent polymer film was quantified experimentally and examined using ray tracing simulation. Spot excitation provided a localized source of photoluminescence. Parallel grooves extracted the light far away from the source. By varying the separation between excitation and extraction sites, the propagation of photoluminescence within the film was analyzed. Simulation was then applied to determine the contribution of scattering to the observed propagation distance. Relying only on the relative light intensities, it provides a robust method to quantify and understand light propagation within polymer films. © *2013 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4800941]

Device efficiency is of crucial importance in developing solid-state lighting. It is defined as the product of the internal quantum efficiency (IQE), related to material quality and light extraction efficiency, related primarily to geometry.[1] Along with quantifying IQE, understanding and enhancing light extraction from light-emitting diodes is thus of crucial importance.[2,3] The majority of research in this latter area has been focused on Gallium Nitride (GaN) system as its high index of refraction results in the majority of luminescence being trapped or guided within the active layer. Various methods have been employed to aid in light extraction such as forming a nanostructured graded-index antireflection layer,[4] embedding photonic crystals,[5] and texturing the active layer.[6] Closely related to light extraction is light propagation within these films. As both propagation and extraction are difficult to quantify experimentally,[1] recent work has focused on the use of simulation techniques such as radiative transfer analysis,[7] finite-difference time-domain (FDTD),[8] and Monte Carlo ray tracing simulations.[9] The latter being used, for example, to investigate the effects of pyramidal texture[10] or implanting pyramidal lens array.[1]

Light propagation and extraction is also of concern for other light-emitting systems such as thin films of luminescent polymers.[11] Despite their lower index of refraction, total internal reflection may trap up to ~75% of the generated luminescence. Clearly understanding light propagation within thin polymer films is crucial in predicting the effects and then optimizing geometry for maximum light extraction.

We introduce a combined experiment and simulation based approach to address the issue of light propagation within thin polymer films. In order to quantify this effect, spot excitation with a focused laser beam was used to provide a localized source for photons (photoluminescence). Periodically spaced parallel grooves provided a means to extract the photoluminescence (PL) far from this point source. By varying the separation between excitation and extraction points, the propagation distance of photoluminescence was quantified. As light propagation within such films is affected primarily by geometry, absorption and scattering (due to impurities or aggregates in the case of polymers), Monte Carlo ray tracing[12] was used to model and thus estimate the mean free distance between scattering events based on the known PL and absorption spectra of the film along with the geometry. As this methodology relies on relative and not absolute intensities, they are independent of both the excitation intensity and point spread function of the excitation beam and the geometry of the extraction groove. It thus provides a robust method to observe and understand light propagation in thin films. Knowledge of the propagation distance of light generated within such films should allow one to optimize dimensions of structures employed to help extract this light.

Weakly absorbing fluorescent thin films were prepared as follows. High molecular weight polystyrene (PS, Mw = 2 000 000 g/mol., polydispersity (DPI) < 1.3, Pressure Chemical) and dissolved in a solvent of equal-parts toluene, tetrahydrofuran, and cyclohexanone and doped with 1% poly[2-methoxy-5-(2′-ethylhexyloxy)-p-phenylene vinylene] (MEH-PPV, Mn ~ 200 000 g/mol, DPI ~ 5, Sigma-Aldrich). Dust and undissolved particles were filtered (0.45 $\mu$m pores) prior to spin-casting on a clean glass. The resulting ~500 nm thick film was floated off on a glass surface, transferred onto a copper grid, and solvent treated to enhance bonding. Films were then stretched uniaxially to produce localized deformation zones (crazes) perpendicular to the stress direction spaced approximately 20 $\mu$m apart in which the film thickness abruptly drops by a factor of three.[13] These were used to extract PL generated. In order to mitigate substrate effects and thus simplify modeling, all experiments were conducted on free-standing films supported by a copper grid.

The experimental setup used for the observation of light propagation in the film is illustrated in Fig. 1. Output from a cw-Argon laser ($\lambda$ = 488 nm, power ~ 1 mW), after attenuation to the nW level, was focused onto the sample using standard microscope high numerical aperture objectives. PL from the film surface was collected by the same lens and separated from the reflected excitation light by a dichroic mirror and long pass filter (Semrock) having a combined optical

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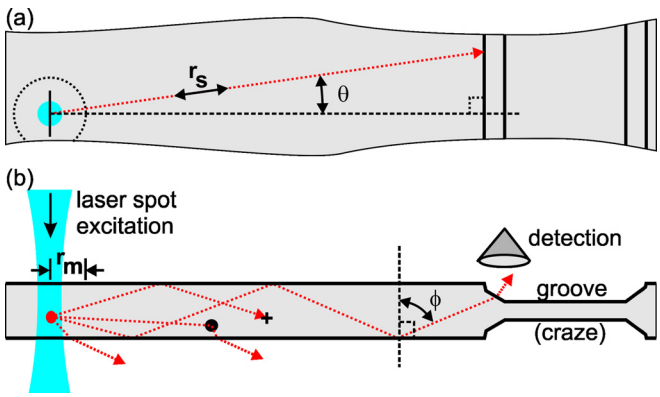


FIG. 1. Schematic of the freestanding thin film under laser excitation. (a) Top view. (b) Side view. The separation ($r_s$) between the laser spot and the groove used to extract PL was varied from 2.5 $\mu$m ($r_m$) to ~20 $\mu$m and the intensity of emission at the craze edge recorded. Four typical trajectories for PL emitted from a single molecule are indicated by the red dotted lines: escape from thin film ($\phi < \phi_c$ (critical angle for total internal reflection), $r < r_m$); propagation and then absorption (+); propagation and scatter (•); propagation and escape from the thin film via a groove.

density greater than eleven at the excitation wavelength. Propagation of excitation light within the film was measured by first photobleaching a single point in the film followed by a confocal scan using a low intensity beam. The propagation of the PL generated within the thin film was observed by varying the separation between the excitation spot and a nearby craze edge ($r_s$). Emission (PL) at the craze edge was detected using an EM-CCD camera (Andor Luca).

To support the experimental results, Monte Carlo based ray tracing[12] was used to model light propagation based on the optical and geometrical properties of the film. Optical inputs included the measured PL and absorption spectra of dilute MEH-PPV[14] and the refractive index (n) of the polymer film (assumed to be equal to that of the PS host (1.57)). The only free parameter was the mean free path or distance between scattering events ($l_s$) which accounts for scattering due to surface inhomogeneities and impurities in the film itself. For simplicity, scattering was assumed to be wavelength independent in the range $\lambda = 525$ nm to $\lambda = 675$ nm. The geometrical inputs were measured (i.e., film thickness, determined using a Dektak 150 surface profiler, location and width of crazes by optical microscopy). Absorbing and emitting dipoles were assumed to be oriented in the plane of the film.[15,16] While not crucial to the work presented here, the detailed structure of the crazes was based on that proposed by Lin[13] and confirmed by AFM measurements. Within the craze regions, the refractive index was set to $n = 1.46$ to take into account the introduction of nanosized voids[17] with the absorption/emission dipoles to be oriented perpendicular to the crazes.[18] Each trace involved, first, following the trajectory of the $\lambda = 488$ nm excitation photon from the time it entered the thin film until it was absorbed or left the film region. In the case of absorption, a new photon was generated (with its wavelength, direction and polarization properties initialized at random based on the known PL spectrum and dipole orientation). This photon was in turn followed until it was either absorbed, scattered, escaped the film, or left the region of interest. Photobleaching of the film was modelled under the assumption that the rate of photobleaching was directly proportional to the intensity of excitation light at a given position in the thin film. For each simulation, a total of 10 000 000 photon trajectories were observed.

In order to characterize the propagation of excitation light within the thin film, the film was partially photobleached by the focused laser spot and then observed using confocal microscopy (at low power, the rate of photobleaching is linearly dependent on excitation intensity). Results are shown in Fig. 2. In the confocal image, Fig. 2 (inset), two crazes (bright lines) are seen along with two partially photo-bleached spots (dark) due to extended spot excitation. Elsewhere, emission from the film is uniform. The main figure displays the intensity profile across one partially photo-bleached film along with that predicted by simulation for a focused $TEM_{00}$ Gaussian beam (FWHM ~ 700 nm). The profile of the partly photobleached region directly represents the profile (FWHM) of the excitation spot indicating that excitation light is either absorbed or passes through the film. There is little or no propagation of excitation light laterally in the plane of the film. This indicates that the source of photoluminescence within the film is limited to the area of direct excitation. Emission from other areas of the film is thus due to propagation of PL generated in the region of spot excitation and not due to confinement and propagation of excitation light.

The propagation of photoluminescence in the thin film was deduced by observing the emission from the crazed film observed by the EM-CCD (Fig. 3) under spot excitation. The left inset shows the PL image of the thin film as recorded on the EM-CCD. In addition to the high irradiance in the directly excited region (bright circular spot), emission also occurs from two crazes (bright vertical lines). These crazes extract light from the film at approximately constant efficiency over an angular range of $\Delta\theta \pm 30°$ perpendicular to the craze direction. Above this angle, emission drops off rapidly due to total internal reflection from the craze edges. In addition, there are a few bright spots

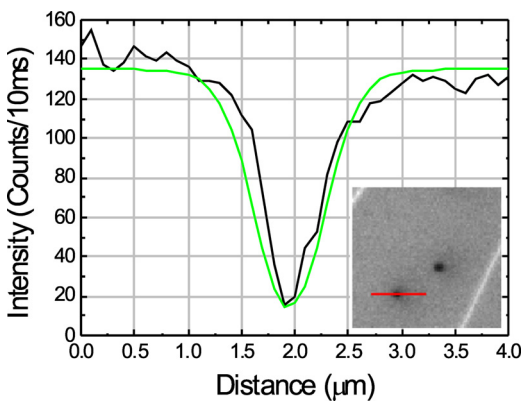


FIG. 2. Profile of photoluminescence (PL) intensity across the region of crazed film photo-bleached by spot excitation denoted by the red line in the inset. The black (green) line is the experimental (simulation) result. (Inset) Confocal PL image taken after extended spot excitation. The two black spots represent areas of the film that were photobleached. These spots correspond to the propagation of the excitation beam in the thin film. Laser power at the sample surface was 2 $\mu$W during photobleaching and 2 nW during the confocal scan.

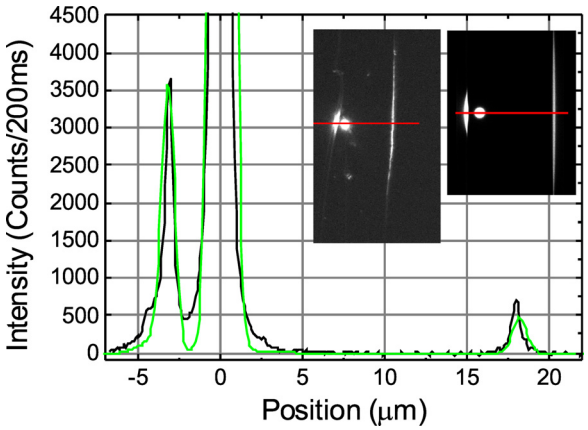


FIG. 3. Intensity of PL emitted from the film under spot excitation as recorded by the EM-CCD camera. (Left inset) Experiment. The bright circle is due to emission from the directly excited region of the film. (Right inset) Simulation. (Main figure) Profile of PL intensity across the film at the location indicated by the red line in the insets. The black (green) line is the experimental (simulation) result. Spot excitation is at 0 $\mu$m.

and additional low-level light emission in other parts of the film due to scattering from impurities or aggregates in the thin film. The relative irradiance can be seen more clearly by observing the profile of the PL intensity through the excitation spot and two crazes. While the PL intensity emitted from the directly excited region is strong, there is also considerable emission both from the nearby craze as well as from one $\sim$16$\mu$m away. For sake of completeness, alongside the experimental results, simulation (discussed later in the text) results are also shown. The simulated image (right inset) is visually similar to the experimental results (left inset). In addition, the relative intensity of emission from the two craze regions is similar to that observed experimentally.

In order to understand the propagation of PL within the film, the excitation spot was moved across the film and the PL irradiance at the craze edge obtained as a function of the separation ($r_s$) between the center of the excitation source and edge of the craze.[19] Intensity as a function of the separation between source and craze edge is plotted in Fig. 4 as black

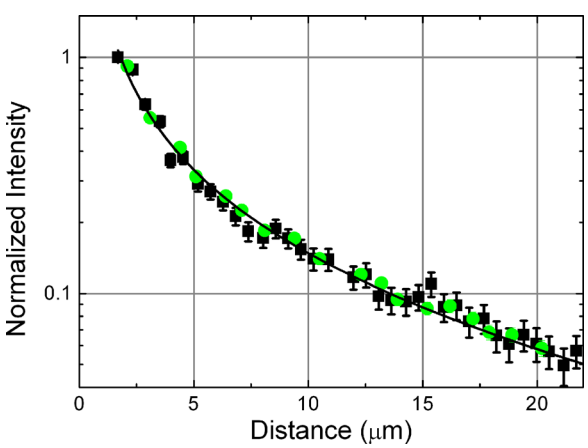


FIG. 4. PL intensity from the crazed region as a function of distance between the excitation spot and craze. Experimental (simulation) results are indicated by black squares (green circles). The black line is the result of fitting the experimental results to an exponential-circular decay curve with $r_o = 40\mu$m. Simulation was conducted using the measured absorption and PL spectra and a scattering length ($l_s$) of 100 $\mu$m.

dots. As can be seen in Fig. 4, the larger the separation, the less light is extracted from the film at any individual point by the craze. This reduction in emission is due to (1) the circular spreading out of PL in two dimensions, (2) self-absorption by the dopant molecules (MEH-PPV) and scattering within the film, and finally (3) the extraction efficiency of the craze. We propose that the PL irradiance from the edge of the craze can be expressed as the product of three terms,

$$I(r_s,\,\theta) = \frac{A}{r_s} \times \exp\left(-\frac{r_s}{r_o}\right) \times T(\theta) \quad if \quad r_s > r_m, \qquad (1)$$

where $r_s$ (cf., Fig. 1) is the separation between the excitation spot and the craze used for light extraction, $\theta$ is the angle of craze relative to the transverse direction of light propagation, and **A** is related to excitation fluence. The first term accounts for the circular spreading of PL, and the final term for the angular dependence of transmission out of the film (T) at the craze interface. For $\theta < \pm 30^\circ$, T is approximately constant. For this work, the key term is the middle term which accounts for the reduction in PL intensity within the film due to the combination of absorption ($\alpha$) and scattering of light out of the beam path ($l_s$). It is characterized by the decay distance ($r_o = 1/\alpha + l_s$). The latter quantity, scattering length or mean free path ($l_s$), is strongly dependent on sample preparation. We note that the above equation is only valid outside the region of direct excitation and where total internal reflection (i.e., $\phi > \phi_c$) dominates ($r_m$). For the 500 nm film here, these conditions are satisfied for $r_s > r_m \sim 2.5\ \mu$m. The result of fitting using this equation is shown as a solid line in Fig. 4 and yields a value of $r_o = 40\mu$m $[-10\mu$m $+ 20\mu$m$]$ for the decay distance.

It is not possible to separate the contributions of absorption and scattering to this decay distance experimentally. While not necessarily trivial, the absorption coefficient for the thin film can be measured. However, it is not possible to do so for the scattering coefficient. In order to quantify the latter, ray tracing simulation, using the measured geometry and optical constants,[14] was employed iteratively. The scattering length was varied until the simulated dependence of the decay of PL irradiance from the edge of the craze as a function of separation ($r_s$) converged to the experimental results. Simulation results for the best fit distance ($l_s = 100\ \mu$m $[-30\ \mu$m $+ 100\ \mu$m$]$) are indicated by the circles in Fig. 4. Good agreement was obtained between experiment and theory. Comparing the mean free path between scattering events with the absorption spectra for MEH-PPV indicates that below $\lambda < 575$ nm self-absorption of MEH-PPV within the film limits the propagation of PL. At progressively longer wavelengths, i.e., above $\lambda > 575$ nm, where MEH-PPV has little or no absorption, it is the relatively weak scattering that limits the propagation of light in the thin film.

In conclusion, the propagation of light within a thin polymer was observed using spot excitation to excite, and crazing to extract, photoluminescence. Ray tracing simulation was used to quantify the amount of light scattering in the thin films. Physically, the scattering length ($l_s$) corresponds to film quality with higher quality films allowing light to travel further due to the elimination of impurities and aggregates within the film. While traditionally a key

objective in spin-casting is to create high quality films with a small scattering coefficient, recent work has shown that by purposely increasing scattering, device efficiencies for Organic Light Emitting Diodes (OLEDs) can be increased up to four times.[20]

We believe that this methodology—spot excitation and light extraction by means of a groove or break in film symmetry—should be helpful in observing and characterizing the propagation of light generated in thin films. As the method relies only on the relative and not absolute intensity of photoluminescence, the results are independent of both the point spread function and intensity of the excitation beam and the extraction efficiency of PL from the groove or inhomogeneity. When combined with ray tracing simulation, it allows the contribution of scattering to be separated from self-absorption. (Note that this work focusing on the micrometer range is complementary to Inami *et al.*'s recently published work making use of electron beam excitation and FDTD simulation to describe light propagation over distances of $<100$ nm.[21])

This research was funded by the National Science Council of the Republic of China (Taiwan).

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