Surface-plasmon-enhanced photoluminescence from metal-capped Alq₃ thin Films

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Absolute quantum efficiencies of surface-plasmon-enhanced photoluminescence from Au capped Alq₃ films were measured using an integrating sphere. The metal “mirror” and directional enhancement effects due to surface roughness which usually occur in forward/backward collection measurements were eliminated using this integrating sphere technique. Up to 40% of the enhanced photoluminescence observed using the forward/backward collection method was shown to have come from mirror and/or enhanced directional scattering effects. Purcell factors obtained from the integrating sphere data and from time-resolved photoluminescence measurements were consistent, confirming surface-plasmon coupling. Incorporating a thin spacer layer enhanced the quantum efficiency and also eliminated nonradiative recombination due to the metal layer. The results clearly show the importance of using an integrating sphere when measuring overall surface-plasmon quantum efficiencies to eliminate directional scattering effects. © 2009 American Institute of Physics. [DOI: 10.1063/1.3190501]

Tris-(8-hydroxyquinoline) aluminum (Alq₃) has been widely used as an emitter for organic light emitting diodes. From the device point of view, achieving high efficiency depends on both the internal quantum efficiency (η), on which radiative excitons have a strong influence, and the external efficiency with which light can be extracted as useful radiation. Recently, surface-plasmon (SP)-mediated emission has been produced from semiconductors and organic films by capping them with a thin layer of metal.^{1–9} When the metal layer is placed within the near-field of the emissive layer and when the energy gap of the semiconductor is comparable to the SP energy at the metal-dielectric surface, resonant coupling to the SP mode greatly enhances the spontaneous recombination rate in the semiconductor. However, with a metal layer present, up to 40% of the device's power is lost to SP modes.⁷ Only a fraction can be recovered and radiated as light. Fortunately, a metal layer with roughness or nanostructure allows SPs to scatter the light out of the emissive layer, yielding high photon extraction efficiency.^{5–7,10}

In most experiments, the photoluminescence (PL) has been collected in the backward or forward direction.^{1,6,7,9} Part of the increase in the luminous intensity may be attributed to reflection of light from the metal “mirror” in the backward direction, and/or to enhanced forward (and backward) scattering of the PL due to the roughness of the metal. Only light within a small emission cone is able to escape into the air at a dielectric/air interface due to total internal reflection. A rough metal surface, however, scatters photons in all directions, which may enhance forward (or backward) emission.

In these cases, the metal mostly enhances the extraction efficiency; it may not contribute much to the SP enhancement. To obtain clear evidence for SP-mediated emission enhancement, the absolute η of uncoated and Au-coated Alq₃

thin films was measured in this study using an integrating sphere. Although enhanced emission of Ag-coated Alq₃ films was observed,⁹ Au coating is more desirable because it is nonoxidizing and commonly used as the electrode material for electronic devices. The dispersion relations of SPs at Au/Alq₃, Au/air, Ag/Alq₃, and Ag/air interfaces were calculated using the Alq₃ dispersion parameters given in Ref. 11 (see Fig. 1 inset). Alq₃ has an emission photon energy of about 2.33 eV. The resonance energy of Au/Alq₃ is much closer to Alq₃'s emission energy than to that of Ag/Alq₃, which again makes Au a more suitable coating material for enhancing the SP resonance of Alq₃ films.

The absolute η , was defined as the ratio of the number of photons emitted from the dielectric film to the number of photons absorbed from the excitation source. The Alq₃ sample was placed inside the integrating sphere, where light

FIG. 1. (Color online) Scanning electron micrograph of a sputtered Au surface on a quartz substrate. The granular surface texture with an average particle diameter of few tens of nanometers can be clearly seen. The inset presents the dispersion relation of a SP at Au/Alq₃, Au/air, Ag/Alq₃ and Ag/air interfaces.

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TABLE I. Absolute quantum efficiencies of uncoated regions (η_d), Au coated regions (η_{d+m}), and Purcell enhancement factors (F_p) calculated using $F_p = (1 - \eta_d)/(1 - \eta_{d+m})$ for films S1–S4. The PL decay lifetimes of the uncoated regions (τ_d), the Au coated regions (τ_{d+m}), and the Purcell enhancement factors (F'_p) calculated using $F'_p = \tau_d/\tau_{d+m}$ for films S2–S4 are also shown.

Film No.	Alq ₃ thickness (nm)	Au thickness (nm)	BCP thickness (nm)	η_d	η_{d+m}	τ_d (ns)	τ_{d+m} (ns)	F_p	F'_p
S1	50	150	0	0.04	0.25			1.28	
S2	100	100	0	0.09	0.20	7.93	5.66	1.13	1.40
S3	100	100	10	0.08	0.45	8.44	7.70	1.66	1.10
S4	100	100	40	0.07	0.27	7.65	4.87	1.27	1.57

emission was redistributed isotropically over an interior surface coated with a diffusely reflecting material. The η was obtained by integrating the measured PL signal over the emission wavelengths. A 325 nm CW light from a He–Cd laser was used for optical pumping. An optical fiber collected the light from the sphere and directed it to an Ocean Optics spectrometer. The response of the fiber and spectrometer detector system was normalized using a calibrated light source.

The PL quantum yields were determined according to the method described by de Mello *et al.*¹² with some modifications taking the absorption of the metal layer into account. Each sample had an Au-capped region while the rest was an uncapped pure Alq₃ surface. The Au was sputtered on the Alq₃ film coated on a quartz substrate. Scanning electron microscopy showed that the sputtered Au surface was granular with an average particle diameter of a few tens of nanometers (see Fig. 1). This granular structure provided the “rough” surface for scattering the SPs into the air. The absorption of the metal layer was taken into account through a control measurement of a sample with only the same thickness of Au coated.

A standard technique for measuring thin-film PL quantum efficiencies with an integrating sphere involves three measurements. For the first measurement, the sphere is empty and laser light (L_a) alone is detected. For the second measurement, the sample is placed inside the sphere and the laser beam is directed onto the sphere wall. The detected signal is composed of scattered laser light from the sphere wall (L_b) and PL emitted after the absorption of scattered laser light (P_b). In the third measurement, the laser beam is directed onto the sample. After the sample absorbs both direct incident light and scattered light, there is a detected signal composed of laser light (L_c) with emitted PL (P_c). α_d , α_m , and α_{d+m} are the fractions of laser light absorbed by the dielectric thin film, the metallic layer, and the dielectric film coated with metal, respectively. Defining the detected laser signals L_c^d , L_c^m , and L_c^{d+m} for the pure dielectric thin film, the metallic layer, and the dielectric film coated with metal respectively, and defining the emitted PL signals P_c^d and P_c^{d+m} for the pure dielectric thin film and the dielectric film coated with metal, respectively, the absolute PL η of the pure Alq₃ can be represented as¹²

$$\eta_d = \frac{P_c^d - P_b(1 - \alpha_d)}{L_a \alpha_d} = \frac{P_c^d L_b - P_b L_c^d}{L_a (L_b - L_c^d)}. \quad (1)$$

Taking the metal layer into account, Eq. (1) can be modified for the case of an Au-coated Alq₃ film to give

$$\eta_{d+m} = \frac{P_c^{d+m} - P_b(1 - \alpha_{d+m} - \alpha_m)}{L_a \alpha_{d+m}} = \frac{P_c^{d+m} L_b - P_b L_c^{d+m}}{L_a (L_c^m - L_c^{d+m})}. \quad (2)$$

Table I shows measured η s of Alq₃ films without and with Au coating. The η_d s of the uncoated regions of the films are about 4%–9%, while the Au-coated regions' η_{d+m} s are about 20%–45%. The PL enhancement due to metal coating was two to six times. The Alq₃ film had not been air sealed and it was exposed to air and moisture for some time before the Au sputtering, thus the η s of the uncoated films were considerably smaller than those normally expected of high quality Alq₃ films.¹³ Indeed, one would like to have a film with lower intrinsic η in order to clearly observe any SP enhancement effect.⁸ The reflection geometry of film S1 was also directly measured, as shown in Fig. 2. A tenfold increase in the PL intensity of Au-coated Alq₃ film was observed in the direct measurements. However, using integrating sphere, the η of Au-coated films was only about six times larger than that of the uncoated films. This suggests that up to 40% of the enhancement observed in the direct measurements came from mirror effects and/or enhanced scattering in the backward direction by the rough Au layer.

Films S3 and S4 had 2,9-dimethyl-4,7-diphenylphenanthroline (BCP) introduced as a spacer between the Au layer and the Alq₃. BCP was added for two reasons. A metal surface can act as a nonradiative trap for excitons, which reduces the radiative recombination rate of excitons and lowers the η . By introducing a spacer of suitable thickness, this trapping effect due to the metal surface can be reduced. Furthermore, a spacer layer provides a mean to study the near field effect with respect to SP coupling. This near field acting on a dipole decreases when the distance between the dipole and the metal is increased. According to Fermi's Golden Rule, the recombination rate (the inverse of the spontaneous decay lifetime τ) is related to the photon density of state and the dipole matrix element, which is proportional to the near field strength.⁴ Using the appropriate metal and spacer layer allows adjusting the near field strength, thus controlling the lifetime τ . It is also known that the η s of a pure dielectric and a metal coated dielectric with SP coupling are $\eta_d = k_{\text{rad}}/(k_{\text{rad}} + k_{\text{non}})$ and $\eta_{d+m} = k_{\text{rad}} + C_{\text{ext}} k_{\text{SP}} / k_{\text{rad}} + k_{\text{non}} + k_{\text{SP}}$, respectively.¹ k_{rad} , k_{non} , and k_{SP} are the radiative, nonradiative, and SP recombination rates, respectively, and C_{ext} is the probability of photon extraction. Assuming that the metal was sufficiently rough that $C_{\text{ext}} \approx 1$ (see Ref. 1 for a discussion), then the Purcell factor is given by $F_p = (1 - \eta_d)/(1 - \eta_{d+m})$. The calculated F_p 's are given in Table I. The measured decay lifetimes of the uncoated and metal coated films can be expressed in terms of

FIG. 2. (Color online) (a) PL of S1, with uncoated (dashed line) and Au-coated (solid line) regions upon laser excitation at 325 nm in an integrating sphere. Detected signals from the incident laser (dotted line), after absorption by the uncoated and the Au-coated regions are also shown at the left of the figure. (b) PL of S1 in direct backward collection geometry. The schematic setup is shown in the inset.

the sum of the recombination rates ($1/\tau_d = k_{\text{rad}} + k_{\text{non}}$ and $1/\tau_{d+m} = k_{\text{rad}} + k_{\text{non}} + k_{\text{SP}}$), so the η increases as the decay lifetime decreases if one assumes C_{ext} close to unity and that k_{SP} is comparable to k_{rad} and k_{non} . Hence the η increases as near field strength increases. The effect can be clearly seen in Table I, where the η_{d+m} of S3 with a thin spacer is larger than that of S4 with a thicker spacer layer. Another point to note is that the η_{d+m} of S2 was comparatively low when there was no spacer between the Alq3 and the Au, but η_{d+m} of S3 and S4 were larger when a thin spacer was included. These results show that metal directly in contact with the emitting organic film causes nonradiative recombination.

The PL decayed nonexponentially, especially for the metal coated samples because there was a large distribution of quenching sites for the amorphous organic films.^{9,14} A $1/e$ decay time constant was calculated for the uncoated and coated region off each sample from the decay curves. Refer to Table I. For every sample, the decay time constant of the Au-coated region, τ_{d+m} , was shorter than that of the uncoated region, τ_d . The Purcell factor $F'_p = \tau_d / \tau_{d+m}$ was adopted for lifetime measurement (Fig. 3).² Taking S2 as an example, it has $\tau_{d+m} = 5.66$ ns, and the enhanced transition rate k_{d+m} was 1.77×10^8 s⁻¹. According to Ref. 9, the transition rates of Alq3 films coated with flat silver and nanotextured silver are

FIG. 3. (Color online) Normalized PL intensity vs time measured by the streak camera for the uncoated (dashed line) and Au coated (solid line) regions of sample S4.

0.91×10^8 and 1.00×10^8 s⁻¹, respectively. These results clearly show that Au coated Alq3 has faster transition rates than Ag coated Alq3, either flat or nanotextured. Table I also shows that the Purcell factors calculated from the integrating sphere data and using the time-resolved method are consistent. The two Purcell factors do not completely agree, but this is understandable since considerable simplifying assumptions have been made when deriving the expressions for F_p and F'_p . Overall, the Purcell factors ranged from 1.1 to 1.7, which indicates that there was an overall enhancement of PL due to SP coupling.

In summary, we have reported absolute η s for Au-coated Alq3 films measured using an integrating sphere. PL enhancement of two to six times was observed. This large enhancement of SP PL achievable by simply sputtering an Au layer on an organic film without the need for any complicated structure has important applications in the design of light emitting diodes.

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