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Electroluminescence efficiency enhancement using metal nanoparticles

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We apply the "effective mode volume" theory to evaluate enhancement of the electroluminescence efficiency of semiconductor emitters placed in the vicinity of isolated metal nanoparticles and their arrays. Using the example of an InGaN/GaN quantum-well active region positioned in close proximity to Ag nanospheres, we show that while the enhancement due to isolated metal nanoparticles is large, only modest enhancement can be obtained with ordered array of those particles. We further conclude that random assembly of isolated particles holds an advantage over the ordered arrays for light emitting devices of finite area. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2957989]

Luminescence enhancement in the presence of metal nanoparticles has been investigated in recent papers.[1,2] The experimental research has been supported by a large body of theoretical work,[3] but to this day there has not been a simple answer to the following question. For an emitter with a radiative efficiency η_{rad}, what kind of enhancement can be achieved with a given metal and what should be the optimal parameters of the nanoparticles. In this work, we shall employ our previously developed model for the surface plasmon polariton (SPP) enhancement of electroluminescence[4] (EL) in conjunction with the "effective mode volume" approach recently developed for the nanocavities[5] to provide a simple analytical model that unambiguously answers the above question. We treat the emission as a two step process. First, the coupling of the material polarization into a closely confined surface plasmon (SP) eigenmode with the rate enhanced by Purcell factor F_P followed by coupling into the radiation continuum. The later coupling has to compete with the nonradiative loss. Usually, the more tightly confined modes that have larger Purcell enhancement have relatively large nonradiative loss, and based upon this tradeoff, we optimize the nanostructure parameters to achieve the best overall enhancement. In our prior work[6] we applied this model to the SPPs on the metal-dielectric interface and have shown that for a given radiative efficiency there exists an optimum SPP mode that is sufficiently well confined, but can still be efficiently coupled into the radiation continuum using a surface grating. Our results also indicated that one can obtain large enhancement only if the original radiative efficiency of the emitter is very small.

In this work, we apply our model to a case that is the extreme opposite of the infinite metal dielectric interface—the case of a single metal nanoparticle and its eigenmode consisting of charge oscillations coupled to the dipole field. At this point, we only consider spherical nanoparticles, but our treatment can be easily modified to other shapes. We then expand this model to ordered array of metal nanoparticles.

First we calculate the effective volume of the nanoparticle SP dipole mode. In the spherical polar coordinate system with z axis perpendicular to the sample plane, we obtain the SP dipole field inside and outside of the metal sphere with a radius a (Ref. 7)

$$\mathbf{E}=\begin{cases} E_0\dfrac{3\varepsilon_D}{\varepsilon_M+2\varepsilon_D}\hat{\mathbf{z}}, & r<a \\ E_0\left(\dfrac{\varepsilon_M-\varepsilon_D}{\varepsilon_M+2\varepsilon_D}\right)\dfrac{a^3}{r^3}(2\cos\theta\hat{\mathbf{r}}-\sin\theta\hat{\boldsymbol{\theta}}), & r>a, \end{cases} \tag{1}$$

we use the Drude-model approximation for the metal dispersion $\varepsilon_M=1-\omega_p^2/(\omega^2+j\omega\gamma)$, where ω_P is the plasmon frequency, γ is the metal loss, and ε_D is the dielectric constant of the surrounding media. Clearly when the condition, $\varepsilon_M(\omega_o)+2\varepsilon_D=0$, is satisfied the field inside the metal sphere remains even in the absence of the outside driving field E_o (polarized in z direction)—a clear indication of an eigenmode oscillating at the resonance frequency $\omega_o=\omega_p/(1+2\varepsilon_D)^{1/2}$. It is easy to see that the maximum field occurs just outside the nanoparticle at $r=a$, where $E_{\max}=6\varepsilon_D E_o/(\varepsilon_M+2\varepsilon_D)$. Assuming that the emission frequency is close to the SP dipole resonance, we obtain the effective mode volume[5]

$$V_{\mathrm{eff}}=\frac{4}{3}\pi a^3\left(1+\frac{1}{2\varepsilon_D}\right), \tag{2}$$

which is very close to the volume of sphere itself.

Since the electron-hole pair states are localized on the scale of the coherent length on the order of a few nanometers at room temperature, the spontaneous emission can be well represented by a classical dipole.[8] Furthermore, the EL in GaN LEDs is typically associated with impurities such as deep acceptor levels.[9] It is therefore appropriate to treat the quantum well (QW) emitter as a pointlike dipole. When this dipole is positioned at a distance d from the metal particle surface and oriented in the direction normal to the surface, the effective density of modes is $\rho_{\mathrm{SP}}=V_{\mathrm{eff}}^{-1}L(\omega)[a/(a+d)]^6$ where the normalized line shape of the dipole oscillation is $L(\omega)=(\gamma_d/2\pi)/[(\omega-\omega_o)^2+\gamma_d^2/4]$—a standard Lorentzian shape. The SP dipole decay rate combines both nonradiative and radiative components $\gamma_d=\gamma_{\mathrm{nrad}}+\gamma_{\mathrm{rad}}$. The nonradiative decay rate can be estimated as $\gamma_{\mathrm{nrad}}=\gamma/2$ from considerations of energy decay of the SP eigenmode inside the metal.

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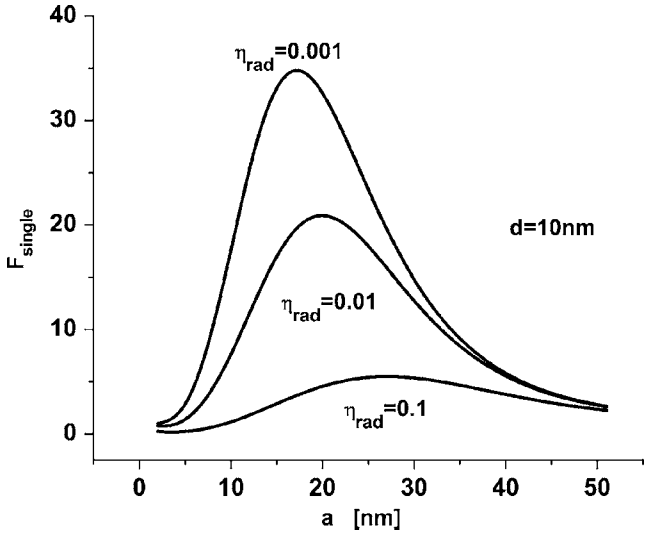

FIG. 1. Enhancement due to isolated Ag spheres on InGaN/GaN QW emitters with a separation of 10 nm as a function of the sphere radius a for different original radiative efficiencies.

The radiative component can be found using the standard dipole radiation power formula[7] with the SP dipole itself given as $p \approx -2\pi\varepsilon_o a^3 E_{\max}$ at resonance as $\gamma_{\rm rad} = \omega_o \chi^3/(1+2\varepsilon_D)$, where the normalized nanosphere radius $\chi = 2\pi a/\lambda_D$ and λ_D is the emission wavelength in the dielectric. It follows that the radiative coupling efficiency of the SP mode is

$$\eta_{pr} = \frac{\gamma_{\rm rad}}{\gamma_{\rm nrad} + \gamma_{\rm rad}} = \frac{Q\chi^3}{1 + Q\chi^3}, \tag{3}$$

where we have introduced the effective Q-factor $Q = 2\omega_o/\gamma(1+2\varepsilon_D)$. The Purcell factor at resonance can be estimated as a ratio of the effective density of the SP modes to that of the radiation continuum taking into account the SP dipole polarized in z direction as

$$F_p = \left[V_{\rm eff}^{-1} L(\omega_o) \left(\frac{a}{a+d} \right)^6 \right] \left[\frac{1}{3\pi^2} \left(\frac{2\pi}{\lambda_D} \right)^3 \frac{1}{\omega_o} \right]^{-1} = \frac{9\varepsilon_D Q}{\chi^3 (1 + Q\chi^3)} \left(\frac{a}{a+d} \right)^6. \tag{4}$$

With this we obtain the expression for the enhancement factor over the original radiative efficiency $\eta_{\rm rad} = (1/\tau_{\rm rad})/(1/\tau_{\rm nrad} + 1/\tau_{\rm rad})$ due to a single metal nanoparticle,

$$F_{\rm single} = \frac{1 + F_p \eta_{pr}}{1 + F_p \eta_{\rm rad}}. \tag{5}$$

The enhancement for the case of isolated Ag spheres and an InGaN/GaN emitter ($Q=5.54$) with $d=10$ nm is shown in Fig. 1. We can see that the enhancement factor exhibits strong dependence upon the nanosphere dimensions with the peak occurring when the radius is small enough to yield smaller effective mode volume for an enhanced Purcell factor, yet is still sufficiently large to assure strong radiative recombination of the SP mode. Another observation that can be made is that the overall efficiency enhancement is much stronger than the one provided by the interface of the dielectric with a metal layer considered in Ref. 6. To understand the origin of this seeming discrepancy we first note that the

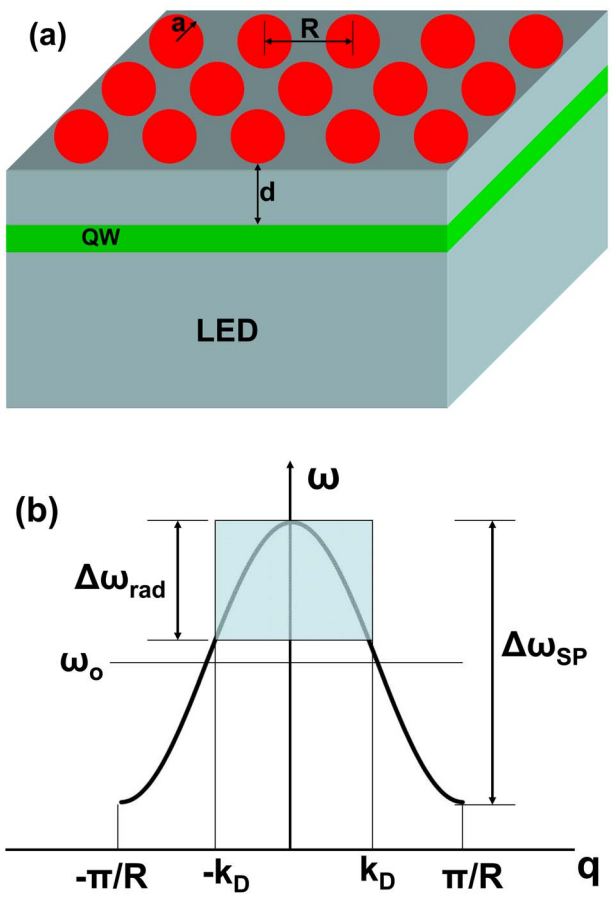

FIG. 2. (Color online) (a) 2D ordered array of metal nanoparticles placed in the vicinity of the QW active region of a LED. (b) Dispersion relationship of the SP modes of the 2D array.

output coupling of the interface SPP is subject to the momentum conservation rules while for the nanosphere SP, these rules do not apply. We also note that a single nanosphere may enhance emission of only a very small emitter, therefore, to achieve practical enhancements for such devices as LEDs one must consider arrays of spheres [Fig. 2(a)]. The eigenmodes of such an ordered two-dimensional (2D) array should be described by a dispersion relationship. It is important to note that although the emission is incoherent, the coherence length $Q\lambda$ is still much larger than the distance between the adjacent nanospheres $R < \lambda$. We can thus use the tight-binding approximation to treat the coupling between the nearest neighboring nanospheres and yield a dispersion relationship

$$\omega_{\mathbf{q}}^2 = \omega_o^2 \left\{ 1 + 2\frac{a^3}{R^3} [\cos(q_x R) + \cos(q_y R)] \right\}, \tag{6}$$

which is a broad SP band in which each mode is characterized by a wave vector $\mathbf{q} = q_x \hat{\mathbf{x}} + q_y \hat{\mathbf{y}}$ as shown in Fig. 2(b). The luminescence gets efficiently coupled into the many modes inside the broad band $\Delta\omega_{\rm SP} \approx 4(a/R)^3 \omega_o$ but only the low wave vector modes with $|q| < k_D = 2\pi/\lambda_D$ within the narrower band ($\Delta\omega_{\rm rad}$) near the top can escape where the eigenfrequency is $\omega_o' = (1 + 4a^3/R^3)^{1/2} \omega_o$. It is easy to see that these radiative modes make up only a fraction of all the SP modes, $g_{\rm rad} = \pi R^2/\lambda_D^2$ ($g_{\rm rad} = 1$, for $R > \lambda_D/\sqrt{\pi}$). Each radiative SP mode, however, is a collective nearly in-phase oscillation of $g_{\rm rad}^{-1}$ SP dipole, and the radiative decay time is decreased by

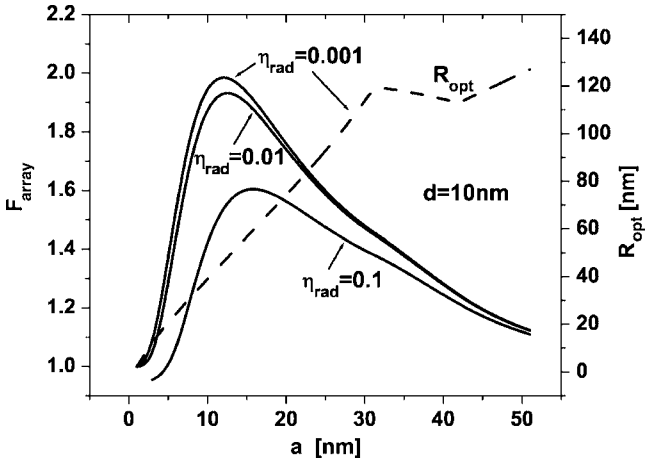

FIG. 3. Enhancement due to 2D array of Ag spheres on InGaN/GaN QW emitters with a separation of 10 nm as a function of the sphere radius a for different original radiative efficiencies. Also shown is the optimized sphere spacing R_{opt} for $\eta_{rad}=0.001$.

about the same factor g_{rad}. The radiative coupling efficiency should then be modified,

$$\eta_{pr} = \frac{\gamma_{rad} g_{rad}^{-1}}{\gamma_{rad} g_{rad}^{-1} + \gamma/2} = \frac{Q\chi^3}{g_{rad} + Q\chi^3}. \tag{7}$$

The remaining modes in the nonradiative band $\Delta\omega_{SP} - \Delta\omega_{rad}$ with $|q| > k_D$ will produce no emission at all. The Purcell factor of these radiative (nonradiative) modes can be calculated

$$F_{P,rad(nrad)} = g_{rad(nrad)} \frac{9\pi\varepsilon_D \gamma Q}{4\chi^3} \bar{L}_{rad(nrad)}(\omega_o') \times \frac{a^6}{[(a+d)^2 + R^2/6]^3}, \tag{8}$$

where the average separation between the emitters and the 2D particles has been considered, $\bar{L}_{rad(nrad)}(\omega_o')$ is the average of the line shape within the radiative (nonradiative) band $\Delta\omega_{rad}$ $(\Delta\omega_{SP} - \Delta\omega_{rad})$, and $g_{nrad}=1-g_{rad}$ is the fraction of those nonradiative modes among total SP modes.

We finally obtain the enhancement of EL by the 2D array

$$F_{array} = \frac{1 + F_{P,rad}\eta_{pr}}{1 + (F_{P,rad} + F_{P,nrad})\eta_{rad}}. \tag{9}$$

For InGaN/GaN QW embedded $d=10$ nm below the metal particles, the enhancement result due to a 2D array of nanoparticles is shown in Fig. 3, where the nanoparticle spacing R has been optimized for each value of a (also shown in Fig. 3). Once again, an optimized particle radius can be obtained

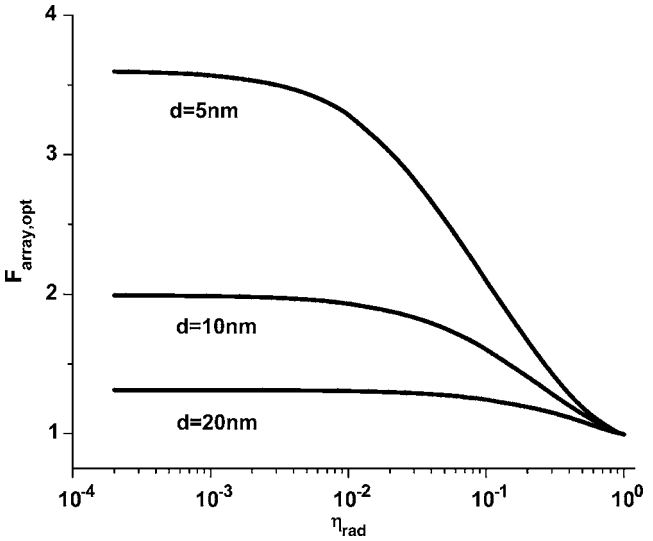

FIG. 4. Optimal enhancement due to 2D array of Ag spheres on InGaN/GaN QW emitter as a function of the original radiative efficiency for several separation values d.

for different original radiative efficiencies η_{rad}. Taking these optimal particle sizes, we plot the result of optimal enhancement as a function of the original radiative efficiency in Fig. 4. In comparison to the result for single isolated nanoparticle shown in Fig. 1, the enhancement is significantly reduced and approaches our previous result of metal-dielectric interface SPP enhancement.[6] It follows that the only way to increase the enhancement would be to introduce strong disorder and localization of SP—but that would lead to broadening of the emission line. We must conclude then that the nanoparticles and their arrays are excellent means of enhancing weak luminescence and Raman processes while their ability to improve performance of relatively efficient emitters, such as light emitting diodes (LEDs), is limited at best.

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