PHYSICAL REVIEW B **66**, 153305 (2002)

Enhancement of spontaneous recombination rate in a quantum well by resonant surface plasmon coupling

Arup Neogi,* Chang-Won Lee, and Henry O. Everitt
Department of Physics, Duke University, Durham, North Carolina 27708

Takamasa Kuroda and Atsushi Tackeuchi
Department of Applied Physics, Waseda University, Okubo 3-4-1, Shinjuku, Tokyo 169-8555, Japan

Eli Yablonovitch
Department of Electrical Engineering, University of California, Los Angeles, California 90095
(Received 28 June 2002; published 4 October 2002)

Using time-resolved photoluminescence measurements, the recombination rate in an $In_{0.18}Ga_{0.82}N/GaN$ quantum well (QW) is shown to be greatly enhanced when spontaneous emission is resonantly coupled to a silver surface plasmon. The rate of enhanced spontaneous emission into the surface plasmon was as much as 92 times faster than QW spontaneous emission into free space. A calculation, based on Fermi's golden rule, reveals that the enhancement is very sensitive to silver thickness and indicates even greater enhancements are possible for QW's placed closer to the surface metal coating.

DOI: 10.1103/PhysRevB.66.153305 PACS number(s): 78.47.+p, 42.50.Ct, 73.20.Mf, 78.55.Cr

The spontaneous emission (SE) decay constant τ for radiating dipoles at $\vec{r}_e$ is given by Fermi's golden rule

$$\frac{1}{\tau}=\frac{2\pi}{\hbar}|\langle f|\vec{d}\cdot\vec{E}(\vec{r}_e)|i\rangle|^2\rho(\hbar\omega), \tag{1}$$

where $\rho(\hbar\omega)$ is the photon density of states (DOS) and $\langle f|\vec{d}\cdot\vec{E}(\vec{r}_e)|i\rangle$ is the dipole emission matrix element. As pointed out by Purcell, SE may be enhanced by altering the photon DOS.[1] For example, the ratio of enhanced to free space emission (the Purcell factor F) has been measured to be as large as 5 in an atomic system by placing the radiating atoms in a high Q, low volume cavity.[2,3] A Purcell factor of up to 6 has been observed from quantum well (QW) and quantum dot emitters in vertical cavity surface emitting laser structures, while an enhancement of 15 has been observed from quantum dots in a microdisk cavity.[4,5] Photonic crystals and distributed Bragg gratings have also been used to enhance the SE rate by as much as a factor of 4.5.[6–8] Such enhanced SE rates, achieved by increasing the photonic DOS in a small cavity, permit lower threshold, higher modulation frequency lasers as well as more efficient light emitting diodes.

The SE rate can also be modified when semiconductor or dye emitters are coupled to a surface plasmon (SP) of a metallic film.[9–12] A single QW can experience strong quantum electrodynamic coupling to a SP mode if placed within the SP fringing field penetration depth. An electron-hole pair in the QW recombines and emits a photon into a SP mode instead of into free space. The degree of SE rate modification for a given wavelength depends on the SP DOS at that wavelength. The strongest enhancement occurs near the asymptotic limit of the SP dispersion branch, the SP "resonance" energy E_{sp}, where the SP DOS is very high. Nonresonant, SP-mediated SE enhancements as large as 6 have been observed from GaAs QW's near thin Ag films.[9] Even greater enhancements are possible for wide band-gap semiconductors whose emission wavelength is coincident with E_{sp}. In this report, time-resolved photoluminescence (TRPL) measurements of a partially silver-coated InGaN/GaN QW directly demonstrate the SP-mediated resonant enhancement of the recombination rate in a semiconductor QW.

An InGaN/GaN QW was used in these experiments, grown by metal-organic chemical vapor deposition on sapphire substrate.[13] Over a 1.5-μm Si-doped GaN buffer layer was grown a 28-nm $In_{0.04}Ga_{0.96}N$ reference layer, a 6-nm GaN layer, and the 3-nm $In_{0.18}Ga_{0.82}N$ QW as shown in Fig. 1. Above the QW was a 12-nm Si-doped GaN cap layer, placing the QW within the fringing field depth of the SP. A layer of silver, ~8 nm thick, was deposited by electron beam evaporation on one half of the sample surface. The other half was left bare to facilitate direct comparison of the silvered and unsilvered results.

The bulk plasmon energy of silver is 3.76 eV, but the SP energy of Ag is lowered by the GaN dielectric constant.[14]

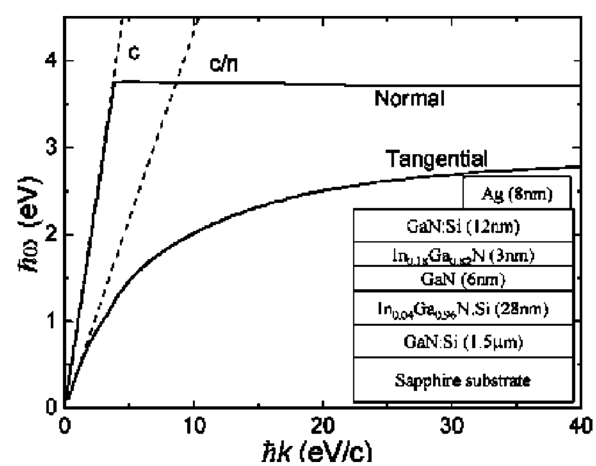

FIG. 1. The calculated surface plasmon dispersion relation for tangential and normal modes. Inset: The structure of the sample studied.

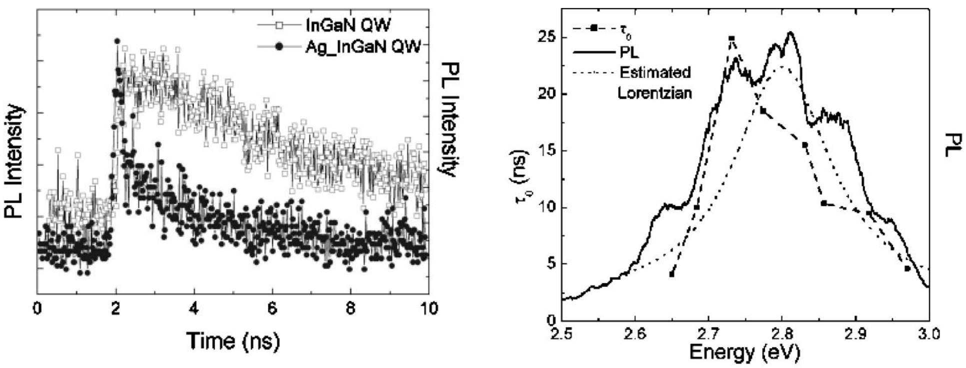

FIG. 2. (a) TRPL decay of the unsilvered and silvered InGaN QW for a 25-nm-wide wavelength detection window (2.79–2.96 eV), with pump energy of 3.14 eV. (b) Comparison of the time-integrated PL and the TRPL-measured recombination rate constant (τ_0) of the unsilvered InGaN QW. The dashed curve is the estimation given by Eq. (4) with $\hbar\omega_c = 2.8$ eV and $\hbar\Delta\omega = 0.16$ eV.

The SP dispersion relation is derived, using Maxwell's equations, from the known dielectric properties of Ag and GaN.[15] Considering a silver film of thickness t and permittivity ε_2, sandwiched between GaN and air with permittivities ε_1 and ε_3 respectively, the boundary condition gives the SP dispersion relation

$$\left(\frac{\gamma_1}{\varepsilon_1}+\frac{\gamma_2}{\varepsilon_2}\right)\left(\frac{\gamma_3}{\varepsilon_3}+\frac{\gamma_2}{\varepsilon_2}\right)-\left(\frac{\gamma_1}{\varepsilon_1}-\frac{\gamma_2}{\varepsilon_2}\right)\left(\frac{\gamma_3}{\varepsilon_3}-\frac{\gamma_2}{\varepsilon_2}\right)e^{-2\gamma_2 t}=0, \tag{2}$$

where $\gamma_i = k^2 - \varepsilon_i\omega^2/c^2$, $i=1,2,3$, and $k=2\pi/\lambda$ is the wave vector. The SP dispersion contains tangential and normal-mode branches (Fig. 1), indicating the dominant direction of current flow in the silver film. For silver films with $t \geqslant 8$ nm, the tangential SP branch asymptotically approaches $E_{sp}=2.85$ eV ($\lambda_{sp}=436$ nm), the SP "resonance" energy. Because the photon DOS is proportional to $dk/d\omega$, the SP DOS and SE enhancement will be greatest at the SP resonance.

The resonant enhancement is measured by comparing the luminescence decay rate from the photoexcited QW on the silvered and unsilvered sides. Room-temperature TRPL measurements were performed using a 100-MHz Kerr-lens mode-locked, frequency-doubled Ti:sapphire (Ti:S) laser with average incident pump power of 10 mW ($\sim$13 μJ/cm^2). The pump excitation energy (3.14 eV or 395 nm) was chosen to be below the band gap of the InGaN reference layer and GaN layers so electron-hole pairs were generated only in the QW. However, defects in the Si:GaN may also emit. The luminescence signal was dispersed in a grating spectrometer (600 g/mm) and measured simultaneously across three wavelength bands (2.55–2.68, 2.71–2.87, and 2.79–2.96 eV) using a Hamamatsu streak camera with a resolution of 15 ps. The three adjacent 25-nm ($\sim$150 meV)-wide wavelength bands spanned the entire continuous-wave photoluminescence (cw PL) emitted from the QW. Features narrower than 25 nm were resolved by sequentially comparing adjacent 5 or 10 nm data windows offset from each other by 1–4 nm steps. Of course, all TRPL traces represent the sum effect of components with wavelength dependent behavior. However, narrowing the bandwidth of the windows further did not significantly improve the ability to measure wavelength dependence because of the reduced signal-to-noise ratio, especially on the silvered side.

An example of a TRPL trace is presented in Fig. 2(a), comparing the temporal decay of the unsilvered and silvered QW PL for a 25-nm-wide wavelength band. The luminescence decay constants from the silvered and unsilvered sides were independently derived from exponential fits to the data (5 or 10 nm windows) and then compared under identical pump and detector parameters. The uncertainty in fitted rate constants for a 10 nm window is 2%–5% at wavelengths near the peak cw PL emission (2.75 eV) and rises to as much as 10%–16% at longer and shorter wavelength extremes where the emission is weaker.

On the unsilvered side, the QW exhibited a long single exponential decay whose decay constant τ_0 was the slowest ($\tau_0=25$ ns) at wavelengths near the peak PL emission (2.76 eV) [Fig. 2(b)]. This very long decay constant, and the correspondingly high PL intensity, indicates a high internal quantum efficiency and insignificant nonradiative processes compared to radiative recombination ($1/\tau_0 = 1/\tau_{nr} + 1/\tau_r \simeq 1/\tau_r$).[16,17] Away from the peak PL emission wavelength, the recombination rate accelerates ($\tau_0 = 4$–5 ns) at the longest and shortest wavelengths measured. The wavelength dependence of InGaN QW emission has been studied previously,[17] and has been found to differ markedly from the SE rate of a dipole radiator (dipole moment d) in a dielectric medium (index of refraction n)

$$\frac{1}{\tau_r(\omega)} = \frac{4nd^2\omega^3}{3\hbar c^3}, \tag{3}$$

especially at low frequency where shallow level traps, impurities, and quantum-dot-like structures in the QW contribute to recombination. A phenomenological estimate is a Lorentzian

$$\frac{1}{\tau_0(\omega)} \simeq \frac{1}{\tau_r(\omega)} = \frac{1}{\tau_{r_0}}\frac{\Delta\omega^2}{(\omega-\omega_c)^2+\Delta\omega^2}, \tag{4}$$

whose peak at (ω_c) and linewidth $\Delta\omega$ also roughly coincide with that of the measured cw PL [Fig. 2(b)].

By contrast, the weaker PL intensity through the silver-coated surface exhibits a biexponential decay. The slower TRPL relaxation component has a decay constant (τ_2) of between 5–10 ns for emission between 2.61–2.94 eV. The decay constant shows no systematic variation with changing emission wavelength and silver thickness. Regarding the latter, the degree of coupling to the SP mode will be shown to depend on the thickness of the silver film. Comparison of the

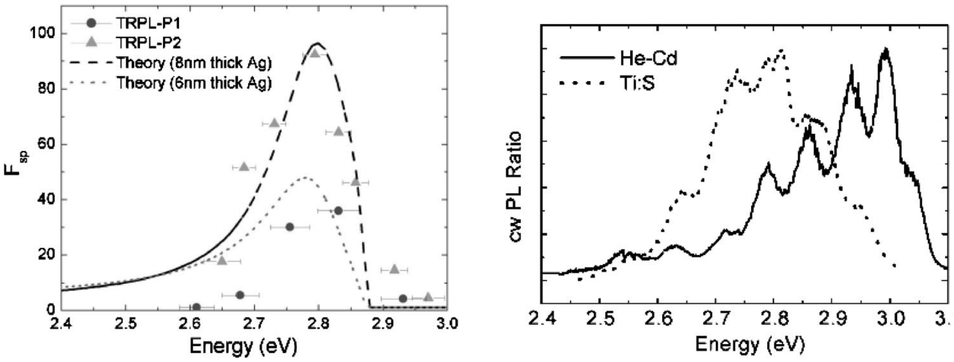

FIG. 3. (a) The Purcell enhancement factor, F_{sp}, measured using TRPL windows 10 nm (position P_1) and 5 nm (position P_2) wide. Overlaid is the prediction of the enhancement. (b) Comparison of the time-integrated PL emission ratios for excitation by HeCd and Ti:s lasers. (The undulations in the cw PL arise from interference in the sample.)

relative cw PL intensities of the InGaN reference layers reveals small variations in the thickness of the silver film. (It is thicker at location P_2 than at P_1.) The fact that τ_2 is insensitive to these thickness variations suggests that the slowly decaying emission must arise from sources uncoupled to the surface plasmon mode, such as impurity bound excitons of shallow level defect states in GaN layers.

The faster decay component, with decay constant τ_1, instead depends sensitively on the thickness of the silver coating and therefore corresponds to enhanced recombination in the QW mediated by the SP mode ($1/\tau_1 = 1/\tau_{nr} + 1/\tau_r + 1/\tau_{sp} \simeq 1/\tau_{sp}$). The measured τ_1 was observed to vary with sample thickness from 235 ps at P_2 to 512 ps at P_1. As expected, this faster component is strongest near E_{sp} (2.85 eV). However, the SP resonance is fairly broad because it is evident at energies 200 meV lower than E_{sp}, and it decays with a time constant almost independent of the emission wavelength. To summarize the wavelength dependence of the SP enhancement, Fig. 3 plots the Purcell factor ($F_{sp} = 1 + \tau_0/\tau_1$) derived from the measured TRPL decay constants. The data demonstrate a sudden rise at higher energies, a peak enhancement near 2.8 eV, and weaker enhancement at lower energies. The maximum values of F_{sp} were 36 (at 2.83 eV) and 92 (at 2.79 eV) at sample positions P_1 and P_2, respectively.

Fermi's golden rule (1) provides insight into the frequency dependence of the Purcell factor and reveals the sensitivity of F_{sp} to the silver thickness t and Ag-QW separation a.[11] First, the electric field of the SP mode at the QW must be calculated and used to derive the dipole matrix element. The SP electric field varies only in the z direction, so the normalization of $E(z)$ to a half quantum of zero-point fluctuation in the dispersive medium becomes

$$\alpha^2 = \frac{S}{A} = \frac{\hbar\omega/2}{\dfrac{A}{8\pi}\displaystyle\int_{-\infty}^{\infty} dz \frac{\partial(\omega\varepsilon(\omega,z))}{\partial\omega}|E(z)|^2}, \qquad (5)$$

where $E(z)$ is the un-normalized electric field at a distance z from the Ag-GaN interface, $|\alpha E(a)|^2$ is the normalized electric field at QW depth a, A is the quantization area, and $\varepsilon(\omega,z)$ is the dielectric function of the GaN, Ag, or air. The enhanced recombination rate ($1/\tau_{sp}$) can then be estimated in the QW under the influence of the local electric field from the tangential SP mode

$$\frac{1}{\tau_{sp}(\omega)} = \frac{2\pi}{\hbar}\left[\frac{1}{3}d^2|\alpha E(a)|^2\right]2\pi k \frac{A}{(2\pi)^2}\frac{dk}{d(\hbar\omega)} = \frac{S}{3\hbar^2}|dE(a)|^2 k\frac{dk}{d\omega}, \qquad (6)$$

where the factor 1/3 comes from spatial averaging of polarization. Inserting measured values for a (12 nm) and t (8 nm) while using the τ_1 data to fit for d (24 nm), the calculation predicts that τ_{sp} should be relatively independent of frequency from 2.6 eV to E_{sp}.

The frequency dependence of F_{sp} derives from Eq. (6) and the frequency dependence of the unsilvered QW recombination rate τ_0 [Fig. 2(b)]. For the parameters in this experiment, the frequency dependence of F_{sp} below E_{sp} derives primarily from τ_0. Unfortunately, a predictive theory of the τ_0 is not available, so an accurate estimate of F_{sp} is not possible. However, if Eqs. (4) and (6) are used as approximations for τ_0 and τ_1, respectively, then $F_{sp}(\omega) \simeq 1 + \tau_0/\tau_1$ may be plotted (Fig. 3) using the parameters for this sample. The predicted frequency peak and width of F_{sp} agree well with the measured peaks and widths of the TRPL data. The peak value of F_{sp} is a sensitive function of Ag thickness through τ_{sp}. A reduction of t from 8 to 6 nm halves the peak value of F_{sp}, suggesting that the differing values of F_{sp} observed at P_1 and P_2 arise from small variations of the Ag thickness.

Recently, F_{sp} was measured in a similar sample by means of cw PL using a HeCd excitation source ($E_{ex} = 3.82$ eV, $\lambda_{ex} = 325$ nm).[11] A ratio of the PL emission for the unsilvered to silvered sides was measured as a function of wavelength, and a peak enhancement factor of 55 was estimated from the data. Those measurements were repeated here, and although the measured enhancement factors were similar to and consistent with the TRPL data, the energy of maximum enhancement in both cw PL measurements was blue shifted from E_{sp}. When time-integrated PL is measured using the Ti:S laser instead, this blueshift disappears (inset, Fig. 3). Note that the HeCd laser excites all layers of the sample while the Ti:S laser only excites the QW and GaN defects. Therefore, any cw PL ratio measured using a HeCd laser must be understood to represent F_{sp} convolved with other excitation-dependent effects (particularly in the cap layer), while the TRPL data measures only F_{sp}. Furthermore, the role of nonradiative recombination was ignored in

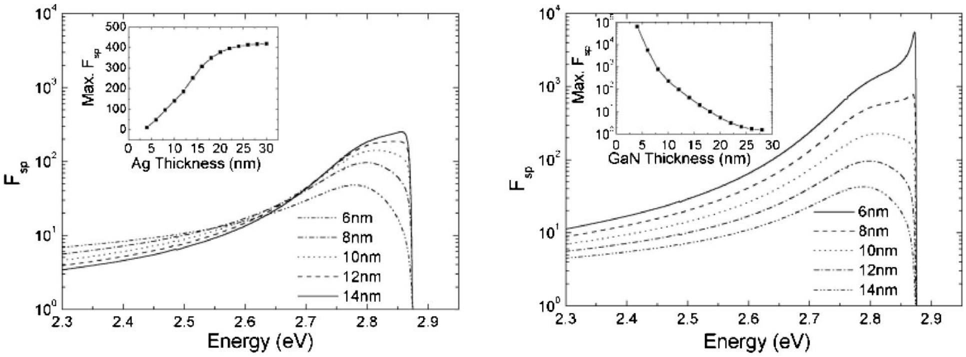

FIG. 4. (a) Calculated F_{sp} for various Ag thicknesses t with Ag-QW separation $a = 12$ nm. Inset: Maximum F_{sp} values for a given t with $a = 12$ nm. (b) Calculated F_{sp} for various Ag-QW separations a with Ag thickness $t = 8$ nm. Inset: Maximum F_{sp} values for a given a with $t = 8$ nm.

that work, leading to an overly simiplistic estimate of F_{sp} based on Eq. (3). The phenomenological estimate (4) includes both radiative and nonradiative effects.

Using Eqs. (4) and (6) to estimate F_{sp}, even larger enhancements are predicted over narrower frequency bands. For a prominent resonance in F_{sp}, Fig. 4 indicates that it is necessary for the Ag film to possess a thickness $\geqslant 6$ nm for a QW 12 nm from the surface. In support of the earlier deduction that the Ag film is slightly thicker at P_2 than P_1, the value of F_{sp} is predicted to increase with increasing film thickness and asymptotically approaches 422 for $t \geqslant 26$ nm ($a = 12$ nm).

The strength and frequency dependence of F_{sp} are even more sensitive functions of the Ag-QW separation, especially for small a. Resonant enhancements of more than 10^4 are predicted for QW's only 4 nm below the surface. These predicted enhancements may actually be conservative because the synergistic "back action" coupling between dipole emitters and SP field, which increases as a decreases, is not included in this calculation. A more comprehensive calculation of this enhancement factor, including the necessary radiation reaction effects, is beyond the scope of this paper. Nevertheless, the enhancement will likely remain broad because inhomogeneous broadening ($\hbar\Delta\omega_{inh} \simeq 100$ meV) will probably limit $\omega_c/\Delta\omega < 30$.

The authors would like to thank S. Kellar, U. Mishra, and S. DenBaars of UCSB for providing the QW sample, and I. Gontijo, M. Boroditsky, and G. Khitrova for useful discussions. This work was supported by the Army Research Office and the National Research Council.

*Email address: arup@phy.duke.edu

[1] E.M. Purcell, Phys. Rev. **69**, 681 (1946).

[2] E.V. Goldstein and P. Meystre, in *Spontaneous Emission and Laser Oscillation in Microcavities*, edited by H. Yokoyama and K. Ujihara (CRC, Boca Raton, 1995), p. 1.

[3] S.M. Dutra and P.L. Knight, Phys. Rev. A **53**, 3587 (1996).

[4] C. Weisbuch, H. Benisty, and R. Houdré, J. Lumin. **85**, 271 (2000).

[5] J.M. Gérard *et al.*, Phys. Rev. Lett. **81**, 1110 (1998); E. Moreau *et al.*, Appl. Phys. Lett. **79**, 2865 (2001).

[6] J. Vučković, M. Lončar, and A. Scherer, IEEE J. Quantum Electron. **36**, 1131 (2000).

[7] M. Borditsky *et al.*, J. Lightwave Technol. **17**, 2096 (1999).

[8] T. Baba *et al.*, J. Lightwave Technol. **17**, 2113 (1999).

[9] N.E. Hecker *et al.*, Appl. Phys. Lett. **75**, 1577 (1999).

[10] T. Baba *et al.*, Jpn. J. Appl. Phys. **35**, 97 (1996).

[11] I. Gontijo *et al.*, Phys. Rev. B **60**, 11 564 (1999).

[12] A. Brilliante and I. Pockran, J. Mol. Struct. **79**, 169 (1982).

[13] S. Keller *et al.*, J. Cryst. Growth **195**, 258 (1998), and references therein.

[14] H. Ehrenreich and H.R. Philipp, Phys. Rev. **128**, 1622 (1962); A. Liebsch, Phys. Rev. Lett. **71**, 145 (1993).

[15] G. Hass and L. Hadley, *American Institute of Physics Handbook*, 3rd ed. (McGraw-Hill, New York, 1972), Chap. 6g, pp. 6–149; D. Brunner *et al.*, J. Appl. Phys. **82**, 5090 (1997).

[16] B. Monemar *et al.*, Proc. SPIE **3624**, 168 (1999).

[17] S. F. Chichibu, Y. Kawakami, and T. Sota, in *Introduction to Nitride Semiconductor Blue Lasers and Light Emitting Diodes*, edited by S. Nakamura and S. F. Chichibu (Taylor & Francis, London, 2000), Chap. 5, pp. 153–270, and references therein.