Chapter 2
Surface Plasmon Enhanced Solid-State Light-Emitting Devices

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Abstract A novel method to enhance light emission efficiencies from solid-state materials was developed by the use of surface plasmon (SP). A 17-fold increase in the photoluminescence (PL) intensity along with a 7-fold increase in the internal quantum efficiency (IQE) of light emission from InGaN/GaN quantum wells (QWs) was obtained when nanostructured silver layers were deposited 10 nm above the QWs. A 32-fold increase in the spontaneous emission rate of InGaN/GaN at 440 nm probed by the time-resolved PL measurements was also observed. Likewise, both light emission intensities and rates were enhanced for organic materials, CdSe-based nanocrystals, and also Si/SiO\textsubscript{2} nanostructures. These enhancements should be attributed to the SP coupling. Electron–hole pairs in the materials couple to electron vibrations at the metal surface and produce SPs instead of photons or phonons. This new path increases the spontaneous emission rate and the IQEs. The SP-emitter coupling technique would lead to super bright and high-speed solid-state light-emitting devices that offer realistic alternatives to conventional fluorescent light sources.

Keywords Plasmonics · Surface plasmon · Polariton · Light-emitting device · InGaN · Quantum well · CdSe · Quantum dot · Silicon nanocrystal

1 Introduction

Conduction electron gas in a metal oscillates collectively and the quantum of this plasma oscillation is called “plasmon.” A special plasma oscillation mode called “surface plasmon (SP)” exists at an interface between a metal, which has a negative dielectric constant, and a positive dielectric material [1]. The plasma oscillation frequency (\omega_{\text{SP}}) of the SP is different to that in the bulk plasmon (\omega_{\text{P}}). The charge
fluctuation of the longitudinal oscillation of the SP, which is localized at the interface, is accompanied by fluctuations of transversal and longitudinal electromagnetic fields, which is called surface plasmon polariton (SPP). Schematic diagram of the SP mode and the SPP mode generated at the metal/dielectric interface is shown in Fig. 2.1a. As the SPP is one of the electromagnetic wave modes, it can interact with light waves at the interface and it brings novel optical properties and functions to materials. The technique of controlling and utilizing the SPP is called “plasmonics” and has attracted much attention with the recent rapid advance of nanotechnology [2–4].

Figure 2.1b shows behaviors of the SPP at a metal/dielectric interface. The wave vector of the SPP \( k_{SP} \) along the \( x \) direction (parallel to the interface) can be written with the following equation when the relative permittivity of the metal is \( \varepsilon_1 = \varepsilon'_1 + \varepsilon''_1 i \) and that of the dielectric material is \( \varepsilon_2 \) [1]:

\[
k_{SP} = \frac{\omega}{c} \sqrt{\frac{\varepsilon'_1 \varepsilon_2}{\varepsilon'_1 + \varepsilon_2} + \frac{\omega}{c} \left( \frac{\varepsilon'_1 \varepsilon_2}{\varepsilon'_1 + \varepsilon_2} \right)^{\frac{3}{2}} \frac{\varepsilon''_1}{2\varepsilon_1^2} i},
\]

(2.1)

where \( \omega \) and \( C \) are the frequency of the SPP and the light velocity in vacuum, respectively. The first term of this equation is known as the dispersion relation of the SPP. Figure 2.2a shows the typical dispersion relations of the SPPs at Al/GaN, Ag/GaN, and Au/GaN interfaces. Usually, the \( k_{SP} \) values are much larger than the wave vector of the light wave propagated in the dielectric media, because \( \varepsilon'_1 < 0 \) at the visible wavelength regions. This fact suggests that the SPP can propagate into nanospaces much smaller than the wavelength. This is one of the most important features of the SPP. This enables us to shrink the sizes of waveguides and optical circuits into nanoscale [5]. \( k_{SP} \) becomes infinity when \( \varepsilon'_1 + \varepsilon_2 = 0 \) and the frequency under this condition is \( \omega_{SP} \). The second term of Eq. (2.1) indicates damping of the SPP mode. Figure 2.2b shows the propagation length \( (L_x) \) of the SPP at Al/GaN, Ag/GaN, and Au/GaN calculated by Eq. (2.1). This figure suggests that the SPP can propagate to a few tens or a few hundreds of micrometers.

Wave vectors of the SPP \( (k_{zj}) \) along the \( z \) direction (perpendicular to the interface) in a metal \( (j = 1) \) or a dielectric material \( (j = 2) \) are given by [1]
Fig. 2.2 (a) Dispersion diagrams of the SPP at Al/GaN, Ag/GaN, and Au/GaN interfaces. (b) Penetration depths and propagation distances of the SPP at Al/GaN, Ag/GaN, and Au/GaN interfaces calculated by Eqs. (2.1) and (2.2), respectively

\[ k_{zj} = \sqrt{\varepsilon_j \left( \frac{\omega}{c} \right)^2 - k_{SP}^2} \quad (j = 1, 2). \] (2.2)

\( k_{zj} \) should be an imaginary number because \( k_{SP} \) is larger than the light line. This suggests that the SPP cannot propagate to the \( z \) direction but decays exponentially. Figure 2.2b also shows the penetration depth (\( d_z \)) of the SPP into GaN at each interface calculated by Eq. (2.2). The \( d_z \) values strongly depend on the wavelength but are always much shorter than 1 \( \mu \)m. This means that the electromagnetic fields of the SPP are strongly localized at the interface and it makes giant fields at the interface. This huge field enhancement effect is also one of the most important features of the SPPs. It has been applied to sensors which have high sensitivities based on the surface plasmon resonance (SPR) at the interface [6]. Moreover, the SPPs can be localized into one-dimensional spaces using metal nanowires. Localized surface plasmon (LSP), which is localized into zero-dimensional spaces using metal nanoparticles, is well known for application of the surface enhanced Raman scattering (SERS) [7]. The LSP nanoprobe enables the optical imaging with super resolution and very high sensitivity [8].

Moreover, several future possibilities of plasmonics have been proposed recently, e.g., the plasmonic metamaterials [9] with negative refractive index at visible regions, the plasmonic therapy for cancer, and the optical cloaking technology [10] based on plasmonics. Undoubtedly, plasmonics becomes a key technology at wider fields and would attract much more attention in the near future. Here, I describe one of the new applications of plasmonics, that is, surface plasmon enhanced light emissions. Recently, I and my coworkers developed a novel method to enhance the light emission efficiencies from solid-state materials by the use of surface plasmon. The technique we invented adds new potential to plasmonics.
2 Background of Solid-State Light-Emitting Devices

Since 1993, InGaN quantum wells (QW)-based light-emitting diodes (LEDs) have been continuously improved and commercialized as light sources in the ultraviolet and visible spectral regions [11]. Moreover, white light LEDs, in which a blue LED is combined with a yellow phosphor, have been commercialized and offer a replacement for conventional incandescent and fluorescent light bulbs [12]. However, these devices have not fulfilled their original promise as solid-state replacements for light bulbs as their light emission efficiencies have been limited. The most important requirement for a competitive LED for solid-state lighting is the development of new methods to increase its quantum efficiency of light emission.

The external quantum efficiency ($\eta_{\text{ext}}$) of light emission from an LED is given by the light extraction efficiency ($C'_{\text{ext}}$) and the internal quantum efficiency (IQE: $\eta_{\text{int}}$). $\eta_{\text{int}}$ in turn is determined by the ratio of the radiative ($k_{\text{rad}}$) and nonradiative ($k_{\text{non}}$) recombination rates of carriers.

$$\eta_{\text{ext}} = C'_{\text{ext}} \times \eta_{\text{int}} = C'_{\text{ext}} \times \frac{k_{\text{rad}}}{k_{\text{rad}} + k_{\text{non}}}.$$ (2.3)

Often, $k_{\text{non}}$ is faster than $k_{\text{rad}}$ at room temperature, resulting in modest $\eta_{\text{int}}$. There are three methods to increase $\eta_{\text{ext}}$: (1) increase $C'_{\text{ext}}$, (2) decrease $k_{\text{non}}$, or (3) increase $k_{\text{rad}}$. Previous work has focused on improving $C'_{\text{ext}}$ from InGaN LEDs by using the patterned sapphire substrates and mesh electrodes [13]. However, further improvements of extraction of light through these methods are rapidly approaching fundamental limitations. Although much effort has recently been placed into reducing $k_{\text{non}}$ by growing higher quality crystals [14], dramatic enhancements of $\eta_{\text{ext}}$ have so far been elusive. On the other hand, there have been very few studies focusing on increasing $k_{\text{rad}}$ [15], though that could prove to be most effective for the development of high $\eta_{\text{ext}}$ light emitters. Here, I describe the enhancement of $k_{\text{rad}}$ by coupling between surface plasmon and the InGaN QWs. If the plasmon frequency is carefully selected to match the QW emission frequency, the increase of the density of states resulting from the SP dispersion diagram (Fig. 2.2a) can result in large enhancements of the spontaneous emission rate. Therefore, energy coupling between QW and SP as described in this chapter is one of the most promising solutions to increase $k_{\text{rad}}$.

Since 1990, the idea of SP enhanced light emission was proposed and received much attention [16–22]. Vuckovic et al. reported the SP enhanced LED analyzing it both theoretically and experimentally [20]. For InGaN QWs, Gontijo and coworkers reported the coupling of the spontaneous emission from QW into the SP on silver thin film and showed increased absorption of light at the SP frequency [21]. Neogi et al. confirmed that the recombination rate in an InGaN/GaN QW could be significantly enhanced by the time-resolved PL measurement [22]. However, in these early studies for InGaN QWs, light could not be extracted efficiently from the silver/GaN surface. Therefore, the actual enhancements of visible light emissions had not been observed directly before our first report.
3 Surface Plasmon Enhanced Light Emission

Recently, we have reported, for the first time, large photoluminescence (PL) increases from InGaN/GaN QW material coated with metal layers [23]. InGaN/GaN single QW (3 nm) structures were grown on sapphire substrates by a metalorganic chemical vapor deposition (MOCVD), and silver, aluminum, or gold layers (50 nm) were deposited on top of the surfaces of these wafers by a high-vacuum thermal evaporation. The sample structure was shown in Fig. 2.3a. To perform the PL measurements, a cw-InGaN diode laser (406 nm) was used to excite the QWs from the bottom surface of the wafer. The excitation power was 4.5 mW. PL was collected and focused into an optical fiber and subsequently detected with a multichannel spectrometer.

Figure 2.3b shows typical PL spectra from InGaN/GaN QWs separated from Ag, Al, and Au layers by 10 nm GaN spacers. For Ag coatings, the PL peak of the uncoated wafer at 470 nm is normalized to 1, and a 14-fold enhancement in peak PL intensity is observed from the Ag-coated emitter. The PL intensity integrated over the emission spectrum is increased by 17 times, whereas 8-fold peak intensity and 6-fold integrated intensity enhancements are obtained from Al-coated InGaN QW. The PL is not increased after Au coating. A small increase in the PL intensity might be expected after metallization because the metal reflects pump light back through the QW, doubling the effective path of the incident light, but differences between Au and Ag reflectivities at 470 nm cannot explain the large difference in the measured enhancement alone. We believe that these PL enhancements should be attributed to the energy transfer between QWs and SPs. The SPs can increase the density of states and the spontaneous emission rate in the semiconductor and lead to the enhancement of light emission by SP–QW coupling. No such enhancements were obtained from samples coated with Au, as its well-known plasmon resonance occurs only at longer wavelengths.

![Sample structure](#)

**Fig. 2.3** (a) Sample structure of InGaN/GaN QW and excitation/emission configuration of PL measurement. (b) PL spectra of InGaN/GaN QWs coated with Ag, Al, and Au. The PL peak intensity of uncoated InGaN/GaN QW at 470 nm was normalized to 1.
We have several evidences to support the contribution of the SPs to obtained PL enhancements. Figure 2.4a shows the enhancement ratios of PL intensities with metal layers separated from the QWs by 10 nm spacers as a function of wavelength. We find that the enhancement ratio increases at shorter wavelengths for Ag samples, whereas it is independent of wavelength for Al-coated samples. The PL enhancement after coating with Ag and Al can be attributed to strong interaction with SPs. The inset figure shows the dispersion diagrams of SP on metal/GaN surfaces (similar to Fig. 2.2a). The surface plasmon frequency ($\omega_{\text{SP}}$) at GaN/Ag is 2.84 eV (437 nm). Thus, Ag is suitable for SP coupling to blue emission, and we attribute the large increases in the PL intensity from Ag-coated samples to such resonant SP excitation. In contrast, $\omega_{\text{SP}}$ at GaN/Au is 2.462 eV (537 nm), and no measurable enhancement is observed in Au-coated InGaN emitters as the SP and QW energies are not matched. In the case of Al, the $\omega_{\text{SP}}$ is 5.50 eV (225 nm), and the real part of the dielectric constant is negative over a wide wavelength region for visible light. Thus, a substantial and useful PL enhancement is observed in Al-coated samples, although the energy match is not ideal at 470 nm and a better overlap is expected at shorter wavelengths. The clear correlation between Fig. 2.4a and the dispersions diagrams suggests that the obtained emission enhancement with Ag and Al is due to the SP coupling.

PL intensities of Al- and Ag-coated samples were also found to depend strongly on the distance between QWs and the metal layers, in contrast to Au-coated samples. Figure 2.2b compares integrated PL enhancement ratios for three different GaN spacer thicknesses (10, 40, and 150 nm) for Ag, Al, and Au coatings. Al and Ag samples show exponential decreases in the PL intensity as the spacer thickness is increased, whereas no such reduction was measured in Au-coated QWs. This
spacer-layer dependence of the PL enhancement ratios matches our models of SP–QW coupling, as the SPP should be localized at the metal/dielectric interface and exponentially decays with distance from the metal surface. Only electron–hole pairs located within the near-field of the surface can couple to the SPP mode, and this penetration depth \( d_z \) of the SP fringing field into the semiconductor is given by Eq. (2.2). \( d_z \) can be calculated as 18 and 63 nm for Ag and Al, respectively. Figure 2.2b shows a good agreement between these calculated penetration depths (lines) and measured values of the PL enhancement (symbols) for Ag- and Al-coated samples.

### 4 Surface Plasmon Coupling Mechanism

We propose a possible mechanism of the QW–SP coupling and the light extraction shown in Fig. 2.5 [24]. First, electron–hole pairs are generated in the QW by photo-pumping or electrical pumping. For uncoated samples, these carriers are terminated by the radiative or nonradiative recombination rates, and the IQE is determined by the ratio of these two rates (Eq. (2.3)). When a metal layer is grown within the near-field of the active layer and when the bandgap energy \( \hbar \omega_{BG} \) of InGaN active layer is close to the electron oscillation energy \( \hbar \omega_{SP} \) of SP at the metal/semiconductor surface, the QW energy can transfer to the SP. PL decay rates are enhanced through the QW–SP coupling rate \( k_{SPC} \), as \( k_{SPC} \) values are expected to be very fast.

![Fig. 2.5 Schematic diagram of the electron–hole recombination and QW–surface plasmon (SP) coupling mechanism](image)

The QW–SP coupling in LED devices may be considered detrimental to the optical efficiency because the SP is a nonradiative wave. If the metal/semiconductor surface were perfectly flat, it would be difficult to extract light from the SPP mode and the SP energy would be thermally dissipated. However, roughness and imperfections in evaporated metal coatings can efficiently scatter SPs as light. However, the SP energy can be extracted as light by providing roughness or nanostructuring
the metal layer. Such roughness allows SPs of high momentum to scatter, lose momentum, and couple to radiated light [25]. The few tens of nanometer-sized roughness in the Ag surface layer can be obtained by controlling the evaporation conditions or by nanofabrication to obtain the high photon extraction efficiencies. Such roughness in the metal layer was observed from higher-magnification scanning electron microscopy (SEM) images of the original GaN surface (Fig. 2.6a) and the Ag-coated surface (Fig. 2.6b). The length scale of the roughness of the Ag surface was determined to be a few hundred nanometers. Similar roughness was also observed from topographic images obtained by shear-force microscopy of the GaN and Ag surfaces shown in Fig. 2.6c, d. We measured a modulation depth of the Ag surface of approximately 30–40 nm while the GaN surface roughness was below 10 nm.

In order to evaluate the SP coupling mechanism that we proposed, we employed a three-dimensional finite-difference time-domain (3D-FDTD) method to represent the coupling processes between electron–hole pairs, SPPs, and photons. To perform 3D-FDTD simulations, we used “Poynting for optics” (Fujitsu Co.) which is known to be very suitable to simulate SP modes [26]. A polarized plane wave with 525 nm wavelength and 1 V/m amplitude was used as a point light source which is an assumption of an electron–hole pair. Figure 2.7 shows the calculated spatial distribution of the electromagnetic field around the Ag/GaN interface. If the point light source was far from the interface, the SPP mode was not excited (Fig. 2.7a). On the other hand, if the point light source was located near the interface, the SPP was well generated and propagated within the interface (Fig. 2.7b). This result suggests that the SPP mode can be generated easily by direct energy transfer from electron–hole pairs without any special structures. Usually, some special configurations are
necessary to generate the SPP mode such as a grating coupler or an attenuated total reflection (ATR) setting to satisfy a phase matting condition between the SPPs and the photons. However, if the light source is located near the metal/dielectric interface within wavelength scale, the SPP mode can be generated regardless of the phase matching condition. The generated SPP mode can be coupled to a photon if there is a nanosized gap structure at the interface (Fig. 2.7c). Then, generated surface plasmon can be extracted from the interface as light and the emission efficiencies should be increased. These calculations support our proposed SP coupling model.

Under the existence of the SP coupling, the enhanced IQE of emission can be described as follows:

$$\eta^*_{\text{int}}(\omega) = \frac{k_{\text{rad}}(\omega) + C_{\text{ext}}'(\omega)k_{\text{SPC}}(\omega)}{k_{\text{rad}}(\omega) + k_{\text{non}}(\omega) + k_{\text{SPC}}(\omega)},$$  (2.4)

where $k_{\text{SPC}}(\omega)$ is the SP coupling rate and should be very fast because the density of states of SP modes is much larger than that of the electron–hole pairs in the QW. $C_{\text{ext}}'(\omega)$ is the probability of photon extraction from the SPs energy. $C_{\text{ext}}'(\omega)$ is decided by the ratio of light scattering and dumping of the SPP mode through nonradiative loss. $C_{\text{ext}}'(\omega)$ should depend on the roughness and nanostructure of the metal surface. If the SP coupling rate $k_{\text{SPC}}$ is much faster than $k_{\text{rad}}$ and $k_{\text{non}}$, the IQE should be dramatically increased.
5 Improvements of IQEs and Emission Rates

Our proposed model suggests that the SP coupling should increase IQEs of emissions. In order to obtain the IQE values to separate the SP enhancement from other possible effects, we have measured the temperature dependence of the PL intensity [23]. Figure 2.8 shows Arrhenius plots of the integrated PL intensities from InGaN QWs separated from Ag and Al films by 10 nm spacers, and compares these to uncoated samples. The IQE values from uncoated QWs were estimated as 6% at room temperature by assuming $\eta_{int} \sim 100\%$ at 4.2 K. These IQE values increased 6.8 times (to 41%) after Ag coating and 3 times (to 18%) after Al coating, explainable by spontaneous recombination rate enhancements through SP coupling. The 6.8-fold increasing of the IQE means that 6.8-fold improvement of the efficiency of electrically pumped LED devices should be achievable because an IQE is a fundamental property and does not depend on the pumping method. Such improved efficiencies of the white LEDs, in which a blue LED is combined with a yellow phosphor, are expected to be larger than those of current fluorescent lamps or light bulbs.

Quite recently, a few groups reported about the SP enhanced LEDs based on our technique. Yeh et al. reported the SP coupling effect in an InGaN/GaN single-QW LED structure [27]. Their LED structure has a 10 nm p-type AlGaN current blocking layer and a 70 nm p-type GaN layer between the metal surface and the InGaN QW layer. The total distance is 80 nm, which is too far to obtain an effective SP coupling. By this reason, they obtained only 1.5-fold enhancement of the emission. Kwon et al. put metal particle on the InGaN QW layer first, and overgrew a GaN layer above the metal particles [28]. However, a large amount of metal particles were gone by high temperature of the crystal growth and only 3% particles remained. Therefore, they obtained only 1.3-fold enhancement of the emission. These tiny enhancement ratios should not be good enough for device application. Therefore, a highly efficient LED structure based on plasmonics is still not yet achieved.

![Fig. 2.8](image_url) Arrhenius plots of the integrated PL intensities of InGaN/GaN QWs with Ag, Al, and uncoated sample with 10 nm GaN spacers. PL integrated intensities at 4.2 K were normalized to 1.
The increased IQE should be due to the enhancement of the spontaneous emission rate. Since the density of states of SP mode is much larger, the QW–SP coupling rate should be very fast, and this new path of a recombination can increase the spontaneous emission rate. We investigated the direct observation of SP-coupled spontaneous emission rate by using the time-resolved PL measurements [24]. To perform time-resolved PL measurements, the frequency-doubled output from a mode-locked Ti:Al₂O₃ laser was used to excite the InGaN QW from the bottom surface of the wafer. The pulse width, wavelength, and repetition rate were chosen as 1.5 ps, 400 nm, and 80 MHz, respectively. A Hamamatsu Photonics C5680 streak camera served as the detector.

Figure 2.9a, b shows the time-resolved PL decay profiles of (a) uncoated and (b) Ag-coated InGaN-GaN QW sample emitters at several wavelengths. All profiles could be fitted to single exponential functions and the spontaneous emission rate ($k_{PL}$) was obtained. The PL decay profile of each sample was quite different and the $k_{PL}$ values of Ag-coated sample were larger than those of uncoated sample. Also, we found that the decay profiles of the Ag-coated sample strongly depend on the wavelength and become faster at shorter wavelengths, whereas those of the uncoated sample show little spectral dependence. We attribute the increase in both emission intensities and decay rates from Ag-coated samples to the SP coupling.

The original spontaneous emission rate is attributed to the radiative and nonradiative recombination rates of the electron–hole pairs in the QW.

$$k_{PL}(\omega) = k_{rad}(\omega) + k_{non}(\omega).$$  \hspace{1cm} (2.5)

By the SP coupling, the spontaneous emission rate should be increased to

$$k_{PL}^*(\omega) = k_{rad}(\omega) + k_{non}(\omega) + k_{SPC}(\omega).$$  \hspace{1cm} (2.6)

Fig. 2.9  (a) Photoluminescence (PL) decay profiles of uncoated InGaN–GaN QW at several wavelengths. (b) PL decay profiles of Ag-coated InGaN/GaN QW at several wavelengths. The distance between the Ag layers and QWs was 10 nm.
The observed $k_{PL}$ and $k_{PL}^*$ values were plotted against wavelength in Fig. 2.10a. The emission rates of Ag-coated sample were much faster than those of the uncoated sample and strongly depend on the wavelength. This difference becomes dramatically larger at the shorter wavelength region. The spontaneous emission rate into the SPP mode (SP coupling rate) depends on the density of states of the SPP by Fermi’s golden rule \cite{16, 17}. The density of states of the SPP mode is proportional to $\frac{dk}{d\omega}$ which can be obtained by the dispersion curve. $\frac{dk}{d\omega}$ is also plotted in Fig. 2.10a as the solid line. The SP coupling rate should be almost equal to the PL decay rate with Ag layers because those values were much larger than the values of the PL decay rate without Ag. Figure 2.10a shows that the wavelength dependence of the SP coupling rates is similar to that of $\frac{dk}{d\omega}$.

Figure 2.10b shows the enhanced IQEs ($\eta_{int}^*$) estimated by the ratios between $k_{PL}$ and $k_{PL}^*$ with Eq. (2.4) under $C'_{ext}(\omega) = 1$. The SP coupling becomes remarkable when the energy is near to the SP frequency described in Fig. 2.2a as 2.84 eV (437 nm). At this shorter wavelength region, the SP coupling rates are much faster than the radiative or nonradiative recombination rates of electron–hole pairs ($k_{SPC} >> k_{rad} + k_{non}$), and the $\eta_{int}^*$ values are reached to almost 100%. Wavelength-dependent $\eta_{int}^*$ values were estimated also from the temperature dependence of the PL intensities (Fig. 2.8) and plotted in Fig. 2.10b (solid line). Both the data show similar behavior. The discrepancy of each data should be due to the light extraction probability from the SPP. $\eta_{int}^*$ estimated by the temperature-dependent measurements of the PL intensities should include the damping energy loss of the SPP. The important fact is that both values are reached to almost 100% at the shorter wavelength region. This suggests one of the most important advantages of the SP...
coupling technique to enhance the emission efficiencies. If we can control the SP frequency and obtain the best matching condition between the emission wavelength and the SP frequency, we can increase both the $\eta_{\text{int}}$ and $C_{\text{ext}}'$ to 100% at any wavelength. It is perfect efficiency and would bring full color devices and natural white LEDs. Tuning of SP coupling should be available by choosing the appropriate metal, metal mixture alloy, multiple layers, or nanostructures. For example, we could improve the green emission of InGaN by fabricating the nano-grating structures of gold layer by E-beam lithography and Ar ion milling [29]. A theoretical study was also reported by Paiella to tune the SP frequency by using metallo-dielectric multiple layers [30].

6 Applications for Organic Light-Emitting Materials

The most important advantage of the SP coupling technique is that the technique can be applied not only to InGaN-based materials but also to various materials. Therefore, we have used this technique for various other light-emitting materials. For example, polymers, appropriately doped with dye molecules, emitting in the visible spectrum provide stable sources of light for displays and illumination sources at a significantly lower cost than semiconductors. Organic light-emitting diodes (OLEDs) have become widely available and are used for replacing inorganic light-emitting diodes as they are less expensive and provide many opportunities with regard to structural placement. Despite the tremendous promise for efficient solid-state lighting offered by such organic light emitters, the road toward spectrally broad white light polymer emitters still holds many design challenges. Thus, it is of both commercial and scientific interest to improve the IQEs of the polymer dyes within such light emitters, as well as to increase the light extraction efficiencies from such organic films. Here, we focus on enhancing the light emission efficiency from organic thin films by using the SP coupling [31].

The experimental setup used to measure our samples is shown in Fig. 2.11a. Dye polymer solution was prepared by dissolving common laser dye molecules of Coumarin 460 in chlorobenzene. This laser dye emits blue light at 460 nm with UV excitation. Then, 2% polymethylmethacrylate (PMMA) was added to the mixture as a host matrix to obtain a 20 mM/L solution of the dye doped polymer solution. Only half of each substrate was metallized, enabling the rapid comparison between polymer emission on top of metal layers with polymer deposited on quartz. After the metallization step, the dye doped PMMA layers were spun onto both gold and silver substrates to obtain layer thicknesses of $\sim$200 nm.

Figure 2.11b shows typical PL spectra of Coumarin 460 on Ag, Au, and bare quartz substrate. While the Au assisted in reflecting the pump laser, the surface plasmons did not seem to couple to the emission wavelength of Coumarin 460 to offer any measurable enhancement. However, we do observe an 11-fold enhancement of the emission light from the Coumarin doped PMMA on silver due the coupling of the surface plasmons generated on the Ag film as the plasmon resonance frequency
closely matches the emission frequency of the dye. Indeed, the dielectric constants for Ag match well with the emission wavelength of Coumarin 460, and if the data with the Coumarin 460 PL intensity normalized to 1. While reflection can be used to account for some of the increased brightness, only the SP coupling can explain the enhancement measured.

Likewise, we obtained obvious enhancements of both PL intensities and emission rates for three conjugated polymers: polyfluorenes (PF)-cyanophenylene(CNP) (1:1), PF-CNP (3:1), and polyfluorenes(PF)-triphenylamine(TPA)-quinoline(Q) [32]. These polymers have been used for OLEDs actually as high-efficient light-emitting materials [33, 34].

7 Applications for CdSe-Based Quantum Dots

CdSe-based quantum dot (QD) nanocrystals are also very promising materials for light-emitting sources. CdSe-based QD nanocrystals possess a number of advantageous features and have been used in LEDs [35, 36] and as biological fluorescent labels [37, 38]. However, their light emission efficiencies are still substantially lower than those of fluorescent tubes. Therefore, we investigate the direct observation of SP-coupled spontaneous emission from CdSe-based QDs [39]. CdSe-based QDs were purchased from Evident Technologies. These QDs have an emission peak around 620 nm and a crystal diameter of approximately 5 nm. The toluene solutions of the QDs were dispersed on quartz substrates. After the solutions evaporated, a monolayer of the QD nanocrystals remained on the substrates. The half parts of the quartz surface were covered by a 50 nm gold layer by thermal evaporation. The sample structure is shown in Fig. 2.12a.

We used two types of nanocrystals: one was naked CdSe nanocrystals and other was CdSe core with ZnS shells (CdSe/ZnS). The IQE of naked CdSe (∼2%) was
well increased for CdSe/ZnS structure (~40%) because generated carriers can be well confined into core/shell structures. Figure 2.12b shows PL spectra of naked CdSe and CdSe/ZnS on gold layers and quartz substrate. A dramatic enhancement in the PL intensity from the QDs on gold layer was very clearly observed for naked CdSe. When the PL peak of the QDs on quartz was normalized to 1, a 30-fold increase of PL intensity was observed. On the other hand, the enhancement of PL intensity of CdSe/ZnS was not remarkable compared with the result of naked CdSe without shells. This fact indicates the merit and demerit of the SP coupling technique for enhancing light emission. The SP coupling increases IQE values by enhancement of spontaneous emission rates. The SP coupling condition is decided by the matching of energies between the SP frequency and the emission wavelength. Thus, the enhancement condition does not depend on the intrinsic IQE values of materials. This feature suggests that the SP-coupling technique is very effective for increasing the emission efficiency of materials with low intrinsic efficiency like naked CdSe, but not so effective for high-efficiency materials like CdSe/ZnS, which were used in this study.

The SP enhanced luminescence of CdSe QDs has been reported by a few groups. Kulakovich et al. [40] reported 5-fold enhancement of the PL intensity for CdSe/ZnS QD and gold colloids. Song et al. [41] achieved ~50-fold enhancement by using CdSe/ZnS QDs and nanoperiodic silver arrays fabricated by electron-beam lithography. Gryczynski et al. [42] reported a well-polarized, directional, and photostable SP coupling emission by using CdSe/ZnS QDs on SiO$_2$/silver thin layers. Compared with these reports, our setup is much simpler and easier. We used naked CdSe and an evaporated gold layer, but we still obtained remarkable enhancement (30-fold). Special geometry or nanoperiodic structures are not necessary for our setup.
8 Applications for Silicon-Based Nanocrystals

The SP coupling technique can be applied to materials that suffer from low emission efficiencies, which include the indirect semiconductor. Usually, the emission efficiencies of such indirect semiconductors are quite low but it is possible to enhance these efficiencies to values as large as those available from direct compound semiconductors by SP enhancement. Accordingly, we tried to enhance emissions from silicon-based semiconductors.

Silicon photonics has attracted a great deal of attention in this decade and is expected as a light-emitting material alternative to compound semiconductors. Several nanostructures such as porous silicon [43], nanocrystals [44], quantum wells [45], and nanowires [46] were fabricated to obtain bright emissions from Si. We tried to enhance emission from Si nanocrystals in SiO$_2$ media with gold thin layers [47]. Silicon nanocrystal QDs were prepared by reactive thermal evaporation of SiO powders in an oxygen atmosphere under vacuum. After rapid thermal annealing, size-controlled Si nanocrystals (∼3 nm diameter) were formed in SiO$_2$ by phase separation. This technique was developed by Zacharias et al. and the details have already been published [48]. Metal thin layers (50 nm) were prepared by thermal evaporation. Figure 2.13a shows a sample structure and Fig. 2.13b shows the PL spectra for Si nanocrystals. A 70-fold large PL enhancement was observed with gold coating at the wavelength region longer than 650 nm, whereas only 2-fold enhancement was obtained from aluminum-coated sample. This should be reasonable because the calculated dispersion diagram of the SP at Au/SiO$_2$ interface suggests that the SP coupling must be effective at a longer wavelength region than 600 nm. On the other hand, the SP at Al/SiO$_2$ is not effective around this wavelength region. It should be effective at much shorter wavelength region.

![Figure 2.13](image-url)

Fig. 2.13 (a) Sample structure of Si nanoparticles dispersed in SiO$_2$ media and excitation/emission configuration of PL measurement. (b) PL spectra of Si/SiO$_2$ with Au, Al, and no metal layer
After our first report of the SP coupling technique, it was already applied to Si nanocrystals and similar enhancements have been reported at room temperature [49, 50]. We measured temperature dependence of PL intensities to estimate the enhanced IQE values [47]. The IQE value from uncoated Si/SiO₂ was estimated as 6% at room temperature by this assumption. The IQE value increased to 36% after Au coating, explainable by spontaneous emission rate enhancements through SP coupling. This value is as large as that of a compound semiconductor with direct transition. However, the emission intensity of Si/SiO₂ was still much weaker than that of InGaN/GaN or CdSe/ZnS with the same IQE value. It was reported that the emission lifetimes of Si/SiO₂ were usually very long (∼ ms) even though some of Si nanocrystals have very high IQE values (>50%) [51–53]. The SP coupling can enhance the emission rate, but the enhanced emissions still have long lifetimes with millisecond scale [49, 50]. These lifetimes are 1,000 times longer than those of InGaN/GaN or CdSe/ZnS which has similar IQE values. The slower emission rates should be the reason for weak emission intensities of Si/SiO₂. The excitation densities of nanocrystals become saturated easily and this brings poor carrier injection efficiencies in spite of their high IQE values. Due to this reason, so far, silicon-based materials are still not useful for light-emitting materials. We believe that both emission rates and excitation densities of Si nanocrystal can be increased by optimizing the SP coupling condition and it would bring super bright silicon LEDs, which could be very cheap to make, easy to process.

9 Conclusions

We conclude that the SP enhancement of PL intensities of light emitters is a very promising method for developing highly efficient LEDs. We have directly measured significant enhancements of IQE and the spontaneous recombination rate. Even when using unpatterned metal layers, the SP energy can be extracted by the submicron scale roughness on the metal surface. A possible mechanism of the QW–SP coupling and emission enhancement has been proposed and highly efficient light emission is predicted for optically as well as electrically pumped light emitters because the mechanism should not be related to the pumping method. Enhanced spontaneous emission should also be very useful for high-speed light-emitting devices for the development of communication technology and optical computing. Moreover, similar plasmonic design should also be applicable to devices based on nonlinear optical materials, photo detectors, waveguides, optical modulators, plasmonic metamaterials, and other optical and electric devices. This technique is very simple and easy, and moreover, can be applicable to various materials that suffer from low quantum efficiencies. So far as we think, the SP coupling may be the only technique with a big possibility of developing the super bright light-emitting devices by the use of the silicon-based semiconductors. We believe that the QW–SP coupling technique would bring super bright plasmonic LEDs, which become the dominant white light source and serve as an alternative to conventional fluorescent tubes.
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References


