Surface plasmon enhanced emission from dye doped polymer layers

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Abstract: We have experimentally verified that the emission of visible light from dye doped polymers can be enhanced with the use of surface plasmon coupling. By matching the plasmon frequency of a thin unpatterned silver film to the emission of a dye doped polymer deposited onto this metal surface, we have observed a eleven-fold enhancement of light emission. By patterning the silver layer, we estimate that the plasmon frequency can be tuned to match dye doped polymer emission frequencies and even larger emission enhancements as well as extraction efficiencies are expected.

OCIS codes: (240.6680) Surface plasmons; (250.3680) Light-emitting polymers

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1. Introduction

The large optical fields provided by surface plasmons have in the past been used to significantly increase the fluorescence and luminescence intensity of dye molecules for applications in biological and biochemical sensing. Molecules can be detected on the surface of metal films or in close proximity to colloidal metal particles by measuring increases in the

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resonant surface plasmon coupled emission [1]. Recently, it has also been shown that plasmon resonances provided by thin metal layers and metal gratings can be designed to increase the efficiency of solid state semiconductor light sources the surface. In such structures, the surface plasmon resonance frequency is tuned to the semiconductor quantum well emission, and the light emission intensity can be increased by over an order of magnitude as nonradiative recombination paths are bypassed through coupling of recombination energy into surface plasmon modes. It is therefore not surprising that similar energy transfer into surface plasmons can also be exploited in the design of more efficient organic light emitters. Recently, the mechanism for emission enhancement through coupling to surface plasmons has been analyzed for InGaN quantum wells [2]. Other enhancement efforts to increase the external quantum efficiencies and increasing the spontaneous emission rates, using surface plasmons, have been reported for semiconductor quantum wells [3-6]. Similar increases in the internal and external quantum efficiencies to those observed in InGaN quantum wells in close proximity to metal surfaces can be obtained from dye-doped organic thin films.

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 [7, 8] (OLEDs) may indeed evolve as the most inexpensive alternatives to fluorescent light sources for large area solid state lighting. Thus, it is of both commercial and scientific interest to improve the internal quantum efficiencies of the polymer dyes within such light emitters, as well as to increase the light extraction efficiencies from such organic films. Indeed, the effect of surface plasmons on the light emission from polymer layers has been recently been investigated by several groups [9-11]. Nanosensors using surface plasmon resonance as well as their applications in conjunction with dye doped polymers or polymer thin films have also been explored [12-14]. Here, we focus on enhancing the light emission efficiency from organic thin films by using the surface plasmon resonance.

2. Experiment

The experimental setup used to measure our samples is shown in Fig. 1. To ensure that only a small amount of the pump light is reflected into the detector, the pump source was introduced at a large incidence angle while the detector was located perpendicular to the sample. We employ an Ocean Optics spectrometer to measure the emission intensity of the organic dye layers. We compare the influence of gold and silver thin films on the light emission of a commonly used laser dye doped in a polymer by using this measurement system. Of course, the light emitting material must be within a few hundred nanometers of the metal surface to benefit from surface plasmon enhancements. For semiconductor quantum wells, this is normally accomplished by growing a very thin spacer separating the quantum well from the metal surface. For polymer layers, it is much simpler to prepare measurable samples, as it is only necessary be ensure that the pump light is not totally absorbed by the dye layer. Most

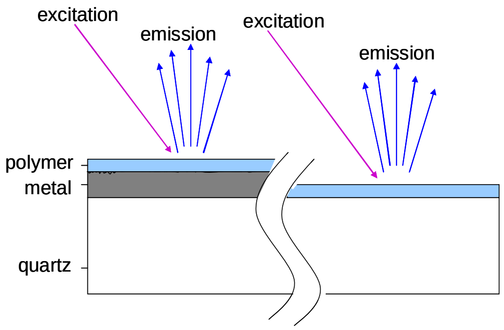

Fig. 1. Sample structure with both pump light and emission light configurations.

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plasmon enhancement measurements conducted on semiconductor emitters have concentrated on backside pumping, through the sample, with the emission light measured also from the back side of the sample [2]. Some other work has measured the optical properties of semiconductors by top side pumping, through the metal, and measuring also from the top side [4, 5]. Combinations of the different pumping and measurement configurations, as well as different angles for the pumped light, have also been pursued [6]. For this paper, it is most convenient to pump through the polymer as well as measure light from the polymer side of the sample.

It is of interest to control both the concentration of the dye material in the polymer as well as the thickness of the polymer. Dye polymer solution was prepared by dissolving common laser dye molecules of Coumarin 460, in chlorobenzene. This laser dye emits blue light at 460nm with UV excitation. Then two percent Polymethylmethacrylate (PMMA) was added to the mixture as a host matrix to obtain a 20mM/L solution of the dye doped polymer solution. Photoluminescence measurements were performed by using a 405 nm InGaN laser diode to pump the Coumarin 460 dye. For the 405nm pump light in Coumarin 460 the absorbance is 0.633[10^{-4} $dm^3mol^{-1}cm^{-1}$]. Our concentration of 2.16 x 10^{-2} moles/L therefore results in an approximate excitation light penetration depth of ~646μm, a penetration depth much larger than the sample thickness of 200nm. To prepare the substrates for the dye doped layers, 50nm thick silver and gold layers were vapor deposited onto quartz substrates at 0.5nm/second deposition rates. Gold and silver layers prepared under these conditions exhibit surface roughness of 30-40nm resulting from the crystal size of the metal layers [2]. 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 ~200nm.

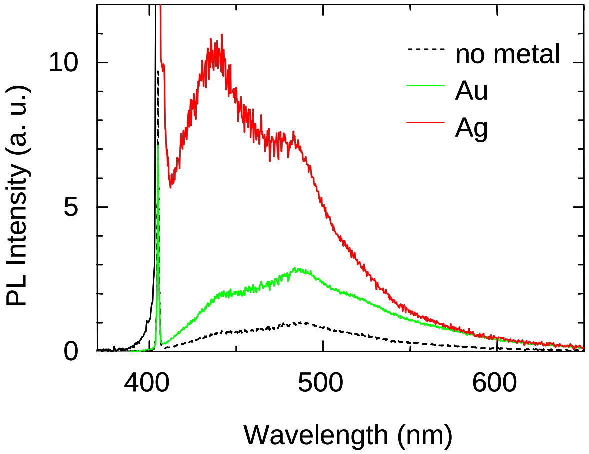

Fig. 2. PL spectra of Coumarin 460 on Ag, Au, and on no metal. Coumarin 460 PL spectra on no metal was normalized to 1.

3. Results and discussion

Figure 2 shows a typical measurement obtained when comparing the spectra of a region with Coumarin 460 doped PMMA spun onto gold with that of the polymer on the bare quartz substrate. While the gold 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 silver film as the plasmon resonance frequency closely matches the emission frequency of the dye. Indeed, the dielectric constants for silver match well with the emission wavelength of

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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.

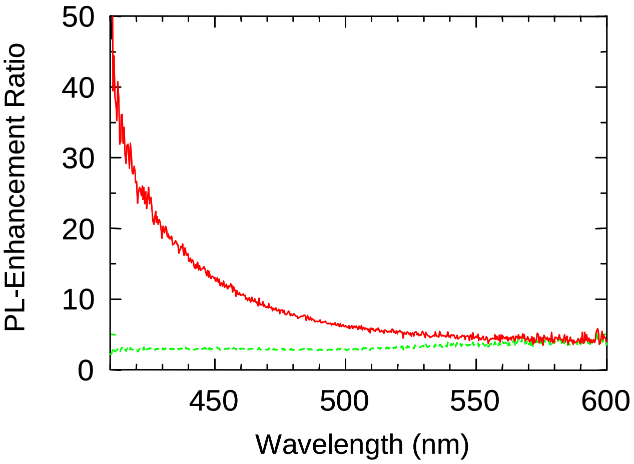

Fig. 3. PL Enhancement ratios demonstrating an increase of enhancement with shorter wavelengths using the silver film. Green dotted line is for gold whereas the red solid line is for silver.

Enhancement ratios illustrated in Fig. 3 further support the notion of SP coupling between the silver and polymer interface. Up to 50 times enhancements are observed along the broad emission spectrum of the dye doped polymer whereas at the peak emission wavelength the photoluminescence enhancement ratio is 11 times. We observed an increase of photoluminescence enhancement ratio with shorter wavelengths for the silver film. However, the PL enhancement ratio is not strongly dependent on the change in wavelength for the gold film.

The dramatic PL enhancement of samples with Ag can be attributed to the strong interaction between the excited dye molecules and SPs. Electron-excited energy of molecules can couple to the electron vibration energy of SP. Then, the molecular relaxation processes may produce a SP instead of a photon, and this new path of the relaxation increases the spontaneous recombination rate. If the metal surface was perfectly flat, it would be difficult to extract light emission from the SP, since it is a non-propagating evanescent wave. However, roughness and imperfections in evaporated metal can scatter SPs as light. The coupling rate between the excited molecular and SP is expected to be much faster than the nonradiative relaxation processes as a result of the large electromagnetic fields introduced by the large density of states.

The phenomenon we exploit here heavily depends on the relationship of the metal dielectric function[15] and that of the polymer. The dielectric constant for PMMA is 2.6 at 1MHz. The surface plasmon dispersion relationship is obtained by using the following equation to calculate the propagation wave number k:

$$k = \frac{\omega}{c}\sqrt{\frac{\varepsilon_1 \varepsilon_2}{\varepsilon_1 + \varepsilon_2}} \tag{1}$$

where ω is the frequency, c is the speed of light, and $\varepsilon_1, \varepsilon_2$ are the real parts dielectric constant of metal and PMMA, respectively. In this equation, the wave number *k* varies with frequency ω. The plot of the surface plasmon dispersion relationship in Fig. 4 is calculated using Eq. (1).

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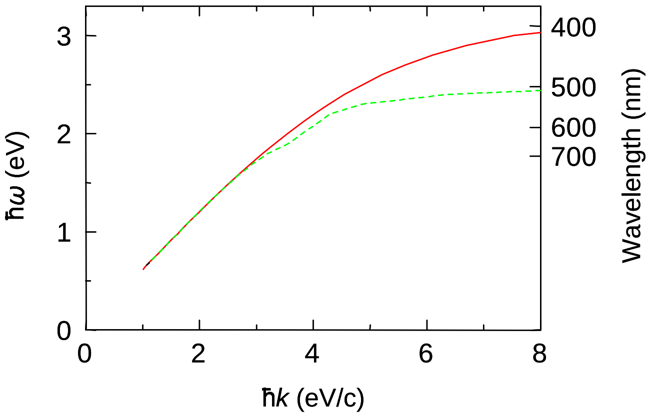

Fig. 4. Dispersion diagrams of surface plasmons generated on Ag/PMMA red solid line and Au/PMMA green dotted line.

The asymptotes of the Ag/PMMA and Au/PMMA surface plasmon dispersion curves closely approach the surface plasmon frequency for silver and gold, respectively. We can therefore determine the energy due to the coupling at the interface of the metal and the polymer. This provides a further explanation for the energy coupling exhibited in the laser dye doped polymer deposited on different metallized substrates. Emission of the Coumarin 460 is closely aligned with the surface plasmon frequency for silver.

Usually, surface plasmons generated at the interface of the metal and the surrounding medium decay exponentially with distance from the metal surface. We can predict the surface plasmon penetration depth (Z) in the polymer from the following equation:

$$Z = \frac{\lambda}{2\pi}\sqrt{\frac{\varepsilon_2 - \varepsilon_1}{\varepsilon_1{}^2}} \tag{2}$$

This penetration depth is 38.6 nm for silver and 23.0 nm for gold, when we substitute the wavelength of the pump light λ. Therefore since our penetration depth in the polymer due to the excitation wavelength and concentration of the dye molecules in the polymer was much longer than the penetration depths of the surface plasmons in the polymer, we could excite every part of the dye molecules adjacent to the metal.

Spacer dependency was explored by fabricating a new sample and first spinning on a 50nm thick non doped polymer layer and baking it at 180 °C to drive off the solvents. This layer was sandwiched between the metal film and the dye doped polymer layer and lowered the coupling efficiency by not allowing efficient enhancement due to surface plasmons. This configuration placed the light emitting material much further away from the metal than the surface plasmon penetration depth mentioned above. Metal dependency trials performed showed that a thinner gold film, around 10nm, had enhanced absorption while a thinner silver film, also 10nm, did not enhance the signal. This result is reasonable based on previously reported calculations [5].

4. Conclusions

We have observed that the emission of dye doped polymers can be enhanced by using surface plasmon coupling to thin metal layers. This study serves as a foundation for the geometric tuning of the surface plasmon resonance and enhancement of the emission of dye polymers using surface plasmons with patterned metal samples. If tuned properly, such lithographically structured layers should provide even higher enhancement values for the dye emission intensity. As the metallic surface can be used as an electrical contact, as a metallic grating for

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enhanced light extraction, and as a mirror for the definition of ultra-small optical cavities to further increase the spontaneous emission rates, we expect that many organic light-emitting diodes could benefit from careful design and choice of metallization. Ultimately, lithographic tuning of the peak emission wavelength and optimization of the polymer layer stack can also result in efficient white light source OLEDs..

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