Enhancement of amplified spontaneous emission in organic gain media by the metallic film

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Abstract

Metallic films were widely used in many micro-cavities or as electrodes. However, the quenching of fluorescent molecules and the large absorption loss of metallic films are generally considered fatal for the lasing. We report the enhancement of amplified spontaneous emission (ASE) of organic gain media in planar waveguide structure with metallic film. Compared to the metal-free device, the ASE threshold of device with metallic film is reduced by 3.7 times by introducing the spacer layer between metallic film and organic gain media. It is found that the radiative decay rate, quantum yield of fluorescent molecules and the net gain of media are enhanced by half-cavity effect of Ag film, which lead to the enhanced ASE and lower lasing threshold.

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1. Introduction

Organic semiconductors are attractive gain media for compact and versatile laser system because these gain media assured wide tenability of wavelength, ease of processing, flexibility, and high efficiency with potentially low cost [1–7]. In the past decades, although all kinds of optically pumped lasers based on organic solid materials were demonstrated, it had not been possible to obtain the stimulated emission under electrical pumping [8–10]. The metal electrodes are usually integrated into the electrical pumping. One of the major challenges for the electrically pumped organic solid lasers is the negative effect of metallic electrode to stimulate emission of organic dyes. The metallic electrodes generally lead to the quenching of the dyes and the large absorption loss, which will be fatal for the lasing [11–13].

In order to evaluate the effect of metallic electrodes on lasing of dyes, the optical pumped organic lasers were usually investigated in presence of metallic electrode. For the planar waveguide structure with metallic film, substantial efforts have been made to reduce the negative effect of metallic film and to restore the amplified spontaneous emission (ASE), such as distributed feedback metallic structure [14,15], low loss metal cladding [13,16–18], and thin spacer of polystyrene or oxidized Ca [18]. In these pervious published works, however, the lasing thresholds for optical pumped devices with metallic films are still higher than the one without metallic film. Therefore, the lasing of organic gain media in presence of metallic films with the lower pumped threshold is desired.

In this letter, we demonstrated an enhanced ASE based on the planar waveguide structure with metallic film. By introduction of a spacer layer between organic gain media and metallic film, the ASE threshold of the device is reduced by 3.7 times compared with that of the device without metallic film. In this works, the presence of the metallic film can provide a half-cavity structure that modified the photonic mode density (PMD). As the results, radiative decay rate and quantum yield (QY) are changed and enhanced, which lead to the improved ASE and lower lasing threshold. To the best of our knowledge, it is the first time to show the ASE of the device with metallic film that

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exhibits the lower pumped threshold than that of the metal-free device.

2. Experiment

In our experiment, the gain media were the blend of Polystyrene (PS), tris(8-hydroxyquinolino)aluminum (Alq3) and 4-(dicyanomethylene)-2-tert-butyl-6(1,1,7,7-tetramethyljulolidyl-9-enyl)-4H-pyran (DCJTB), in which PS is the host inert material, Alq3: DCJTB is the gain media which is a typical donor–acceptor reported in previous published [19,20], Alq3 is used as donor and DCJTB is used as acceptor. There exists a large overlap between the photoluminescence (PL) spectrum of Alq3 and the absorption spectrum of DCJTB which guarantees the perfect energy transfer between Alq3 and DCJTB.

We then prepared the device with the configuration: Glass/Ag film/SiO2/PS:Alq3:DCJTB, which is shown in Fig. 1. On the glass substrate, the Ag film was thermally evaporated under a vacuum of 1 × 10^{-5} Pa at the rate of 0.3 nm/s, then SiO2 layer was deposited onto the Ag film by vacuum sputtering. And then, the chloroform solution with the blends (PS:Alq3:DCJTB = 200: 100: 3.5, wt%) was spin-coated on the SiO2 layer with the speed of 3000 rpm under ambient conditions, the spin-coated films were annealed at 110 °C for 10 min.

In the experiment, as for the configuration of Glass/Ag film/SiO2/PS:Alq3:DCJTB, the thickness of the blended layer of PS:Alq3:DCJTB was 300 nm, the thickness of Ag film was 100 nm, and the different thicknesses of SiO2 layer were employed to show the different ASE behaviors. The thickness and refractive index of the films were measured with Ellipsometer (SE MF-1000, Korea). The PL lifetimes were measured by streak camera. PL quantum yields (PLQYs) were measured by an absolute photoluminescence quantum yield measurement system (Hamamatsu C11347). The devices were pumped by a Nd:YAG laser (355 nm/5.55 ns/10 Hz) (Surelite I, Continuum Corp., USA). Through a pinhole filter, a slit and a cylindrical lens, the laser beam was formed as a stripe with the size of 7 mm × 1 mm, and was perpendicular to the surface of the devices. Edge emission spectra were measured by Fiber Optic Spectrometer (Ocean Optics SpectraSuite, USB2000). The ASE threshold, peak intensity and Full Width at Half Maximum (FWHM) were measured. All measurements were carried out under ambient environment.

3. Results and discussion

For comparison, the device without Ag film, the structure of Glass/PS:Alq3:DCJTB (300 nm), was prepared as the reference. Fig. 2 shows the edge-emission spectra and output intensity of reference device as a function of the pump energy intensity. As reported and in the previous reports [1,2], the neat gain media film exhibits an obvious ASE behavior. When it is pumped by laser pulses with low energy, it exhibits a broad spontaneous emission spectrum and the FWHM is 80 nm. Once the excitation energy becomes large enough, the emission spectrum collapses to a much narrower emission with FWHM of 10 nm. The ASE threshold is then determined.

To study the effect of Ag film on ASE, we prepared devices with the metallic film shown in Fig. 1, in which different thicknesses of SiO2 layer were used as spacer layers, and deposited between the gain media film and the Ag film. Fig. 3(a)–(f) show the edge-emissions of the devices as Fig. 1, the thicknesses of SiO2 layer are 0 nm, 20 nm, 50 nm, 80 nm, 110 nm and 150 nm, respectively. As the reference device, all the devices with Ag film present the characteristics of ASE. At low excitation energy, the devices exhibit the broad spontaneous emission spectra with FWHMs over 80 nm, and when the excitation energy reaches ASE threshold, the spectra suddenly become narrow, the FWHMs reduce to about 8 nm. In Fig. 3(g), we can find that the ASE thresholds change with different thicknesses of SiO2 layer. It shows that with the increasing of the SiO2 thickness, the ASE threshold reduces at first and then increases. The lowest ASE threshold is found when the SiO2 thickness of device is 80 nm. For the corresponding device of Glass/Ag film (100 nm)/SiO2 layer (80 nm)/PS:Alq3:DCJTB (300 nm) (Device A), the ASE threshold decreases to 8.2 µJ/cm², which is reduced by 3.7 times...
Fig. 3. The emission spectra of the device Glass/Ag film (100 nm)/SiO$_2$ layer/PS:Alq$_3$:DCJTB. The thicknesses of SiO$_2$ layer are (a) 0 nm, (b) 20 nm, (c) 50 nm, (d) 80 nm, (e) 110 nm and (f) 150 nm. (g) Dependences of the emission intensities on the pump energy intensity for the devices Glass/Ag film (100 nm)/SiO$_2$ layer/PS:Alq$_3$:DCJTB with different thicknesses of the SiO$_2$ layer. The inset shows ASE thresholds for the devices with different thicknesses of SiO$_2$ layer. The thresholds are 43.4, 14.2, 12.4, 8.2, 10.8 and 18.8 $\mu$J/cm$^2$ when SiO$_2$ thicknesses are 0, 20, 50, 80, 110 and 150 nm, respectively.
compared with ASE threshold of the reference device. The tendency of ASE threshold is shown in the inset of Fig. 3(g), the thresholds are 43.4, 14.2, 12.4, 8.2, 10.8 and 18.8 \text{ l}J/cm^2 when the SiO\textsubscript{2} thicknesses are 0, 20, 50, 80, 110 and 150 nm, respectively. When the thickness of SiO\textsubscript{2} layer is 0 nm, ASE threshold is larger than that of the reference device. This increasing of ASE threshold could result from the quenching of dyes by the metal, which had been reported by other groups\cite{11,13}. However, when SiO\textsubscript{2} layers are introduced as spacer layer between the gain media and metallic film, the ASE is enhanced and a lower threshold than that of the reference device is achieved.

In addition, the device with structure as Ag film (100 nm)/Glass (1.1 mm)/PS:Alq\textsubscript{3}:DCJTB (300 nm) (Device B) was also fabricated. Fig. 4 shows emission intensities as a function of pump energy intensity for the reference device, Device A and Device B. The spectral properties of Device B are similar to that of reference device, showing the ASE threshold of 12.4 \text{ l}J/cm\textsuperscript{2}. We can find that the ASE threshold of Device B is reduced by 2.5 times compared with that of the reference device. A significant improvement of ASE performance by introducing Ag film can be found in Fig. 4.

In order to fully demonstrate the ASE characteristics of the device with Ag film, the gains of the waveguides were also studied in detail. The net gain was measured by using the usual variable-stripe-length method\cite{21}, which was employed to characterize gains of devices with different thicknesses of SiO\textsubscript{2} layer. This method involves the detection of ASE emission from the film edge as a function of excitation length. For the case of ASE, the output emission \(I(\lambda)\) should obey the following equation\cite{22}:

\[
I(\lambda) = \frac{A(\lambda)I_p}{g(\lambda)} \left( e^{g(\lambda)L} - 1 \right)
\]

where \(A(\lambda)\) is a constant related to the cross section for spontaneous emission, \(I_p\) is the pump intensity, \(g\) is the net gain coefficient, and \(L\) is the length of the pumped stripe. Fig. 5(a) shows the ASE intensities of different samples, each as a function of excitation length at 40 \text{ l}J/cm\textsuperscript{2} pump influence. The experimental data, the solid curves in Fig. 5(a), are then fitted with Eq. (1), giving net gains of 6.31, 35.7, 40.2, 46.4, 42.1 and 28.01 cm\textsuperscript{-1} for the SiO\textsubscript{2} thicknesses with 0, 20, 50, 80, 110 and 150 nm, and 30.6 cm\textsuperscript{-1} for the reference device without Ag film. Fig. 5(b) shows the gain as a function of the spacer thickness between the gain media film and the Ag film. It shows that with the increasing of the SiO\textsubscript{2} layer thickness, the gain increases at first, and then reduces. The maximum of net gain is achieved when thickness of SiO\textsubscript{2} film is 80 nm.

In order to further study the effect of Ag film on the ASE enhancement of the devices in Fig. 1, the PL lifetime, PLQY, radiative decay rate of gain media for the devices (with and without Ag film) with different thicknesses of spacer layer were investigated in detail as follows.

In Fig. 6(a), the time-resolved PL decays for the devices (with Ag film) with different thicknesses of SiO\textsubscript{2} layer are shown, Fig. 6(b) shows the lifetimes of dye molecules with and without Ag film as a function of different thicknesses of SiO\textsubscript{2} layer. For the devices with Ag film, the lifetimes are 1.86, 2.08, 2.02, 1.83, 2.0 and 2.19 ns when the SiO\textsubscript{2} thicknesses are 0, 20, 50, 80, 110 and 150 nm, respectively. We can found that when the thickness of SiO\textsubscript{2} layer is 0 nm, it has a short lifetime which results from the quenching of dyes by the metal, which had been reported by other groups\cite{11,13}. However, when SiO\textsubscript{2} layers are introduced as spacer layer between the gain media and metallic film, the ASE is enhanced and a lower threshold than that of the reference device is achieved.
quenching of dyes by the metal. When the SiO₂ layers with the thicknesses above 20 nm are introduced as spacer layer between gain media and metallic film, with the increasing of the SiO₂ thickness, the lifetime reduces at first, then increases, and there is a minimum for the device with 80 nm spacer. For all the devices without Ag film, the lifetimes of dyes are invariable as reference device with 2.32 ns, which are all higher than that of the dyes with Ag film. 

Radiative ($\gamma_r$) and non-radiative ($\gamma_{nr}$) decay rates can be obtained by the measurement of fluorescence lifetime ($\tau$) and PLQY ($q_0$), which is determined by $\tau = 1/(\gamma_r + \gamma_{nr})$ and $q_0 = \gamma_r/(\gamma_r + \gamma_{nr})$, respectively. Fig. 6(d) and (e) show the radiative and non-radiative decay rates of dye molecules with and without Ag film as a function of different thicknesses of SiO₂ layer. We can found that radiative decay rates have a same tendency with that of the PLQYs for the devices with and without Ag film as Fig. 6(d) shows. In Fig. 6(e), we found that for spacer thicknesses larger than 20 nm, the non-radiative decay rate is lower when using the Ag film. In general, the quenching of fluorescence molecules will be dominant when the dye contact with metal surface, which leads to the greater non-radiative rate of dyes. If the spacer is introduced between the dyes and Ag film, the quenching will be restrained, when the thickness of spacer is over 20 nm.

Fig. 6. (a) The time-resolved PL decays for the devices (with Ag film) with different thicknesses of SiO₂ layer. (b) The lifetimes of dye molecules with and without Ag film as a function of different thicknesses of spacer layer. The theoretical simulation of the fluorescence lifetimes for the devices (with Ag film) with the different thicknesses of spacer layer (solid line), the experimental data of the lifetime for the different thicknesses of spacer layer with (circle) and without (square) Ag film are shown. (c) The PLQYs. (d) Radiative decay rates, and (e) non-radiative decay rates of dye molecules with and without Ag film as a function of different thicknesses of spacer layer.
the quenching would be avoided, which leads to the decrease of the non-radiative decay. Additionally, the presence of the Ag film can provide half-cavity structure, which modified the PMD. Changes in PMD act principally to alter the radiative decay. The increasing of the radiative decay rate would lead to the decrease of the non-radiative decay rate [23,24]. These results of Fig. 6 shows that the minimum of lifetime and maximum of PLQY and radiative decay rate are achieved when thickness of SiO₂ film is 80 nm, and for this case, the lowest ASE threshold is found.

The change of lifetime (radiative decay rate) of fluorescence molecules results from the modification of PMD by the microcavity, known as Purcell effect [25]. In our work, the Ag films play a role of reflection surface, and consist of a half-cavity structure. In the half-cavity, the lifetime of fluorescence molecules was modified as reported in previous literatures [23–28]. According to the previous theoretical model [25,27–28], as for the devices in Fig. 1, we discussed the lifetime of fluorescence molecule in detail. We assumed that the dipole orientation was isotropic. Any dipole orientation may be considered as a combination of perpendicular (subscript \( \perp \)) and parallel (subscript \( || \)) dipole components. The parameters of decay rates for these two orientations are found to be [28]:

\[
\begin{align*}
\dot{b}_\perp &= 1 - \frac{3q}{2} \Im \int_0^\infty R^2 e^{-2i\lambda} \frac{u^3}{l_1} \, du \\
\dot{b}_|| &= 1 + \frac{3q}{4} \Im \int_0^\infty \left[ (1-u^2)R^2 + R^4 \right] e^{-2i\lambda} \frac{u \, du}{l_1}
\end{align*}
\]

where \( R^0 (R^\perp) \) is the Fresnel reflection coefficients for the incident ray polarized parallel (perpendicular) to the plane of incidence (p-polarized/s-polarized), \( q \) is the radiative quantum efficiency. The parameter \( u \) is the component of the wave vector in the plane of the interface, and \( l_j = -i(\varepsilon_j / \varepsilon_0 - u^2)\lambda/2 \), the dielectric permittivities are given as \( \varepsilon_1 = n_1^2 \) and \( \varepsilon_2 = (n_2^2 + ik_2)^2 \), where \( n_1 \) is refractive index of SiO₂, \( n_2 \) and \( k_2 \) are the real and imaginary parts of the refractive index of metal.

In this case, the lifetime \( \tau \) is given by [28]:

\[
\tau(d) = \frac{2}{3} \left[ \frac{2}{3} \dot{b}_\perp + \frac{1}{3} \dot{b}_|| \right]^{-1}
\]

\[
d = \frac{2\pi}{\lambda} n d_{1} = \frac{2\pi}{\lambda} (n_1 d_1 + n_3 l)
\]

where \( n_3 \) is refractive index of gain media, \( d_1 \) is thickness of spacer, \( l \) is the distance between fluorescent molecule and the interface between gain media and SiO₂ layer.

The lifetime of dye molecules in front of Ag film as a function of the spacer thickness between gain medium and Ag film is given by:

\[
\tau(d_1) = \frac{1}{T} \int_0^T \tau(d) \, dl = \frac{1}{T} \int_0^T \tau \left( \frac{2\pi}{\lambda} (n_1 d_1 + n_3 l) \right) \, dl
\]

where \( T \) is the thickness of gain media. Eqs. (2)–(7) allow us to calculate the fluorescence lifetime of the device with the different thicknesses of spacer layer, which is shown in Fig. 6(b) with the solid line. In Fig. 6(a) and (b), we found that the experimental lifetimes of fluorescence molecules with different spacer thicknesses between gain media and metallic film agreed very well with the theoretical results. So we can conclude that the enhancement of ASE results from the modification of PMD by half-cavity with the Ag film, which leads to the increased radiative decay and higher QY of fluorescent molecules.

4. Conclusion

In summary, the way to avoid the negative effect of metallic film on the lasing of organic dyes has been an important issue for the electrical pumping. Here, we have demonstrated a performance enhancement of ASE in the optically pumped planar waveguide structure with the metallic film by optimizing the thickness of spacer layer between metallic film and organic gain media. The ASE threshold of device with metallic film is reduced by 3.7 times compared with that of metal-free device. We found that the radiative decay rate and QY of fluorescent molecules are enhanced by half-cavity effect of Ag film and net gain of media is also increased. These was expected to the enhance ASE and lower lasing threshold. To the best of our knowledge, it is the first time to show an ASE of the device with metallic film which has the lower pumped threshold than that of the metal-free device.

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