Effect of different metal-backed waveguides on amplified spontaneous emission*

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We investigate the effect of a metallic electrode on the ability for poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene] (MEH-PPV) film to undergo amplified spontaneous emission (ASE). The threshold of the device with Ag cladding is about 10 times greater than that of a metal-free device, but metal such as Al completely shuts off ASE. The ASE recurs when a thin spacer layer, such as a few nanometers of SiO_2, is introduced between the MEH-PPV film and the Al cladding. Compared with the Cu or Al electrode, the Ag cladding is most suited to serve as an electrode with its low optical loss due to its high work-function and reflectivity.

Keywords: polymer semiconductor, amplified spontaneous emission, electrode

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1. Introduction

Recently, semiconducting conjugated polymers have become attractive gain media for amplified spontaneous emission (ASE) and lasing devices due to their broad spectral emission range, good luminescence qualities, and easy processing from solution.[1−4] These merits suggest that it should be possible to construct compact electrically pumped lasers using polymer materials if the lasing threshold can be made sufficiently low.[1−10] However, substantial effort has been made to optimize the thresholds of optically pumped lasers, but thus far it has not been possible to obtain ASE under electrical pumping.[10−17] One reason for this is that a metallic cathode needs electrons to be injected into. This is a problem because the large absorption loss of metal at optical wavelengths inhibits lasing.[10] In the drive towards developing an electrically driven polymeric lasers, it is important to demonstrate that an optically pumped laser can operate in the presence of a metal. Here, we focus on the nature of the metal electrode used in conjugated polymer-based optoelectronic device.[11] In particular, we show different metal contacted structures, which are critical to high current injection in conjugated polymer-based diodes.

In this work we demonstrate that the ASE is possible in the presence of a metal electrode in slab geometry. And we explore the influence of ASE from the metal contacted waveguide based on MEH-PPV and discuss the factor responsible for the effect of a metal electrode on ASE.

2. Experiment

We chose high-quality poly[2-methoxy-5-(2'-ethylhexyloxy)-1,4-phenylene vinylene] (MEH-PPV), one of the most well-studied semiconducting polymers.[9−11,13−15] We spun 7-mg/ml solutions of MEH-PPV in toluene onto pre-cleaned glass substrates at 1500 rpm to produce films with thicknesses $\sim$ 170 nm at the 500-nm absorption maximum. After spin coating, the spin-coated thin films were dried in a vacuum at 80 °C for 1 h to drive off any excess solvent. We then prepared samples into two structures: glass/MEH-PPV/M and glass/MEH-

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PPV/spacer/M, where M =Ag, Al, or Cu and "spacer" is a thin layer of SiO_2, and the SiO_2 layer thickness is 100 nm. The metals were thermally evaporated in a vacuum of 2×10^{-3} Pa to give a metal layer thickness of ~ 100 nm.

The devices were optically pumped at 500 nm by an optical parametric oscillator (OPO), itself pumped by a Q-switched neodymium ion-doped yttrium aluminum garnate (Nd^{3+}:YAG) laser. The YAG laser delivered 5-ns pulses at a repetition rate of 10 Hz. The pulse energy incident on the sample was adjusted by inserting a neutral density filter into the beam path. The details of our measurement setup are described elsewhere. The emitted light was collected from the edge of the MEH-PPV film and focused into an ACTTON 150 spectrograph through a cut-off filter.[9]

3. Results and discussion

Figure 1 shows the absorption, photoluminescence, and ASE spectra of the MEH-PPV. The thin film exhibits a broad absorption band peaking at 500 nm and a structured PL emission with peaks at 580 nm and 620 nm. The overlap between the absorption and emission spectrum is small, leading to low self-absorption. This is helpful for amplification of spontaneous emission (SE) because low self-absorption reduces low waveguide loss in MEH-PPV. The spectral narrowing takes place at the vibronic side-emission band (0–1) instead of the main emission band (0–0) of the spectrum of MEH-PPV.[9]

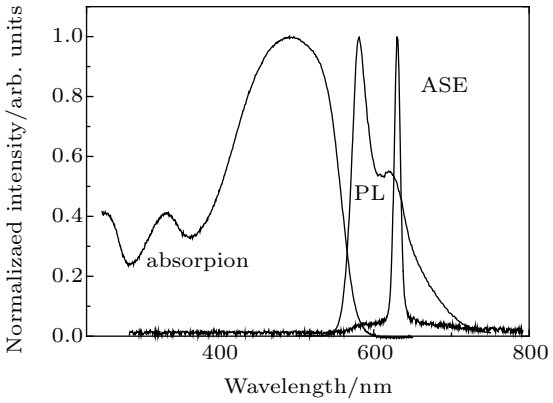


Fig. 1. Normalized absorption, photoluminescence, and ASE spectra of MEH-PPV.

Figure 2 shows the output light intensity and the full width at half maximum (FWHM) of the emission spectrum on the pump energy intensity from the device in glass/MEH-PPV/metal and compares the ASE characteristics for different structures. For the Al-backed MEH-PPV film, the emission intensities increase slowly with the pump intensity increasing. However the Ag-backed and Cu-backed film show an abrupt change in the slope. The threshold pumped energy for ASE can be easily discerned at 0.7 μJ/pulse and 1.4 μJ/pulse for Ag-backed and Cu-backed films, respectively. For Ag-backed and Cu-backed devices, above the threshold, spectral gain-narrowing quickly sets in yielding 620-nm emission with FWHM of 8 nm. However, for the Al-backed device, the spectrum narrowed to an FWHM is not observed. The narrow spectra occur from the device with Ag and Cu electrode at an excitation energy of 6 μJ/pulse, but the Al electrode completely shuts off ASE at the same excitation energy.

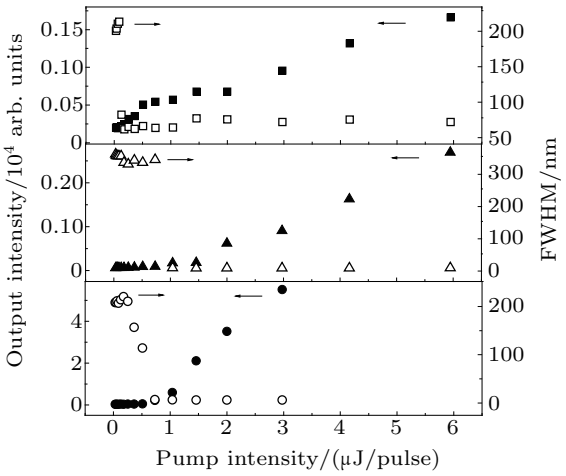


Fig. 2. Dependences of the output light intensity (solid figure) and the full width at half maximum (FWHM) (open figure) of the emission spectrum on the pump energy intensity from the device in glass/MEH-PPV/metal, Cu (square), Al (triangle), or Ag (circle).

It is found that high-work-function metal such as Ag or Cu has some effect on the ASE threshold, but low-work-function metal such as Al completely shuts off the ASE. It is clear that the Ag and Cu do not destroy the gain behaviours of the MEH-PPV films, which is consistent with other studies in which these metals are used in some structures for optically pumped conjugated polymer-based laser.[11] Villers and Schwartz[11] reported that a chemical interaction of the low-work-function metals with polymer, which does not take place with high-work-function metals, causes quenching of ASE.

To investigate the other reasons for the ASE quenching introduced by the electrodes except work function, an SiO_2 layer was deposited by electron

beam evaporation in 9×10^{-4}-Pa vacuum on the MEH-PPV layer and then the electrode was thermally evaporated with a shadow mask on the SiO_2 layer in vacuum. The emission spectra collected from films of MEH-PPV with top layers, each as a function of the 500-nm excitation energy of 6 μJ/pulse, are compared in Fig. 3. It is clear that ASE is reinstated when a thin spacer layer, such as a 100-nm SiO_2layer, is introduced between the MEH-PPV film and the Al cladding. Here SiO_2 layer was used as a cladding material because the refractive index of SiO_2 is 1.49, which is lower than that of MEH-PPV ($n = 1.77$), so that it is easy to form a waveguide structure. SiO_2 with a higher band gap also acted as an insulating layer preventing exciton from quenching on the electrode.[9] Furthermore, from Fig. 3 it can also be seen that the emission spectra of metal clad device has undergone an obvious blue shift compared with that of the SiO_2/metal clad device, which may be attributed to the change in energy band of exciton by metal electrode. Emission peaks from SiO_2/metal clad devices are consistent with those of neat MEH-PPV waveguide. It can prove that the SiO_2 layers prevent excitons from quenching on the electrode.

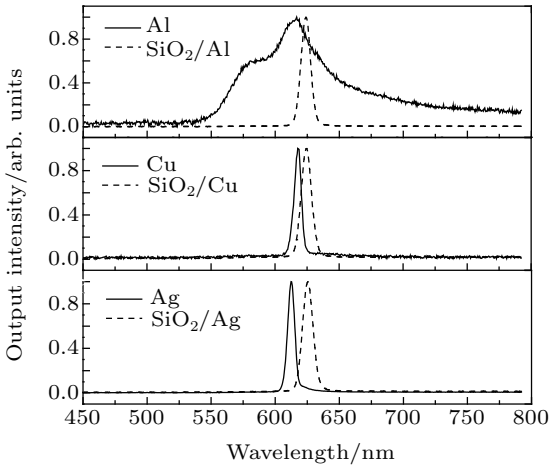


Fig. 3. Emission spectra of metal-backed MEH-PPV films (black curve) and SiO_2/metal backed MEH-PPV films (dashed curve).

In order to be able to compare the ASE threshold behaviours quantitatively, we estimate the actual excitation density for each structure as stated above. Figure 4 shows that output emission intensities integrated over all wavelengths, each as a function of the pump intensity, for metal-free MEH-PPV film and metal-backed MEH-PPV films. It can be seen that the metal layer affects the emission spectrum of the MEH-PPV film strongly. Obviously, the emission spectra of the MEH-PPV films are different from different devices. For the SiO_2/metal clad device, the ASE threshold of Ag device is better than those of the Al and Cu, and the ASE threshold of Al device is better than that of Cu device. The thresholds of these devices are 77, 98, and 103 nJ/pulse, respectively. Their reflectivities are 94%, 83%, and 73%, respectively.[18] A decrease in ASE threshold is detected when the reflectivity index increases.

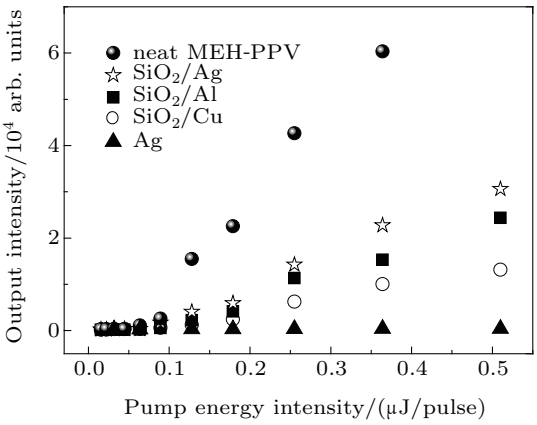


Fig. 4. Output emission intensities integrated over all wavelengths, each as a function of the pump intensity for metal-free MEH-PPV film and metal-backed MEH-PPV films.

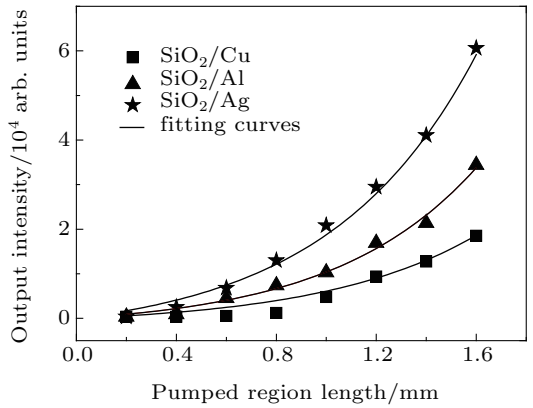


Fig. 5. Dependences of emission intensity at the peak wavelength on the excitation length at indicated pump intensities for metal-backed MEH-PPV films at 0.7 μJ/pulse pump intensity.

In order to fully demonstrate the ASE characteristics of the metal-clad devices, the gains of the waveguides were also studied in detail. The net gain was measured by using the usual variable-stripe-length method, which was employed to characterize gains of SiO_2/metal-backed MEH-PPV films with Ag, Cu, and Al. 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:[1,2,9]

$$I(\lambda) = \frac{A(\lambda)I_{\rm p}}{g(\lambda)}(\,{\rm e}^{g(\lambda)L} - 1), \qquad (1)$$

where $A(\lambda)$ is a constant related to the cross section for spontaneous emission, $I_{\rm p}$ is the pump intensity, g is the net gain coefficient, and L is the length of the pumped stripe. Figure 5 shows the ASE intensities of three samples, each as a function of excitation length at 0.7 μJ/pulse pump intensity. By fitting the experimental data to Eq. (1), the net gain coefficient can be obtained. For the Ag clad device, the net gain is ∼ 77 nJ/pulse. For the Al clad device, the net gain is ∼ 98 nJ/pulse. For the Cu clad device, the net gain is ∼ 103 μJ/pulse. These results are consistent with the reflection rates of the different metals.

Table 1. Amplified spontaneous emission characteristics of metal-free MEH-PPV film and top layer MEH-PPV films.

Top layer	$I_{\rm th}$/nJ·pulse^{-1}	Gain/cm^{-1}	Reflectivity	Peak/nm	FWHM/nm	Work function/eV
Metal-free	65.80	31.02	···	623.12	8.90	···
Al	···	···	···	616.75	69.11	4.20
Cu	1420.26	···	···	617.72	6.22	4.65
Ag	719.02	···	···	612.34	6.53	4.64
SiO_2/Cu	103.13	16.26	0.73	624.56	9.48	···
SiO_2/Al	97.81	17.50	0.83	624.07	8.80	···
SiO_2/Ag	77.02	21.27	0.94	625.54	9.56	···

The ASE parameters of the metal-backed MEH-PPV films with different thicknesses and the metal-free MEH-PPV film are summarized in Table 1. Low-work-function cathode metals such as Al, completely suppress the ability for the polymer to undergo ASE due to absorption loss by the metal. High-work-function metals such as Ag or Cu increase the ASE threshold from 65.80 nJ·pulse^{-1} to 719 nJ·pulse^{-1} or 1420 nJ·pulse^{-1}. The threshold of the device with Ag cladding is ∼ 10 times greater than that of a metal-free device, but metal such as Al completely shuts off ASE. The intensity quenching is attributed to the diffusion of excitons generated in the organic film to the organic/metal interface and their dissociation at the interface.[11] The use of thin SiO_2 layers can restore ASE in the presence of metals. And the ASE threshold from SiO_2/metal contacting is close to that of the neat MEH-PPV film. The fact that SiO_2 layer improves the ability for device to undergo ASE suggests that optical loss by polaron absorption is the primary mechanism by which ASE is shut off. The high reflectivity electrode enhances ASE characteristic.[11] Thus, our results provide an implication to choose the electrode according to the work-function and reflectivity of the metal.

4. Conclusion

We report on a detailed study of the ASE characteristics of metal-backed MEH-PPV films with different structures, showing that the introduction of the metal layer indeed affects the ASE performance of the MEH-PPV film. It is found that the threshold of the device with Ag cladding is ∼10 times greater than that of a metal-free device, but metals such as Al completely shut off ASE. ASE is recurred when a thin spacer layer, such as a few nanometers of SiO_2, is introduced between the MEH-PPV film and the Cu or Al cladding. Compared with the Cu or Al electrode, the Ag cladding is most suited to serve as an electrode for the low optical loss due to its high work-function and reflectivity.

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