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Stimulated emission in the film of polymer/dye blend

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Abstract

Optically pumped stimulated emission behavior in an organic film was demonstrated in this study. The gain material consists of a laser dye perylene doped into polystyrene (PS) matrix in an appropriate weight ratio. The sample was transversely pumped by the three harmonic output of a mode-locked Nd:YAG laser. The change of the emission spectra showed a clear threshold action and gain narrowing phenomenon when increasing the excitation intensity. Three emission peaks were observed below the excitation threshold, which are located at 446, 475 and 506 nm, respectively. However, only the gain narrowing peak centered at 475 nm could be detected above the threshold. The spectra narrowing observed results from the amplified spontaneous emission (ASE) in the gain material.

Keywords: Stimulated emission; Amplified spontaneous emission; Wave-guide; Gain narrowing

1. Introduction

Since 1992 laser action was achieved for the first time in the liquid state of semiconducting polymer (MEH-PPV) operating in the yellow/red wavelength region [1], many groups have directed towards the realization of the laser in the polymer solid film. Up to now optically pumped lasing action had been investigated in various structures, such as F–P(Fabry–Perot) microcavities [2–4], wave-guide and double-heterostructure [5,6], microring [7,8] and microdisk [9]. Additionally, optically pumped stimulated emission from 20 μm crystal grain domain, instead of the conventional amorphous film, in the annealed film based on oligo(p-phenylene) was achieved [10]. Now, the latest challenge in this field of research is the development of an electrically pumped polymer laser. All these progresses showed the interests in the investigation of laser behavior in the organic gain materials. In this report stimulated emission was studied in the perylene/PS film pumped optically.

2. Experiment

The blend of perylene/PS with the mass ratio of about 100:1 was dissolved completely in tetrahydrofuran (THF) for ten hours. The samples were prepared by spin-coating from the THF solution onto polished quartz substrate. The thickness of the films was about 600 nm. The third harmonic output (355 nm) of a mode-locked Nd:YAG laser was used as the excitation source. The pulse width was about 300 ps. The repetition rate was 2 Hz. The pump beam was focused onto the sample using a cylindrical lens ($f = 10$ cm) to obtain an excitation area in the form of a 10×0.2 mm^2 stripe. The emission of the film was detected from either the front or the edge of the film. The experimental schematic was shown in Fig. 1. The sides of the sample were polished to make the edge of the film smoothly and sharply, because it is very important for the coupling of the emission out of the film. The fluorescence spectrum of pure perylene solution was measured with a 960 Spectrofluorophotometer. The refractive index of the film was measured by prism coupling method. All these experiments were performed in the air at room temperature.

3. Result and discussion

The fluorescence spectrum was achieved from whether the side or the surface of the perylene/PS film at a low excitation pulse energy of 0.1 μJ, as shown in Fig. 2. The inset showed the fluorescence spectrum of the perylene in a dilute THF solution with the concentration of 0.03 mg/ml. It was shown that there are three emission peaks in the spectra,

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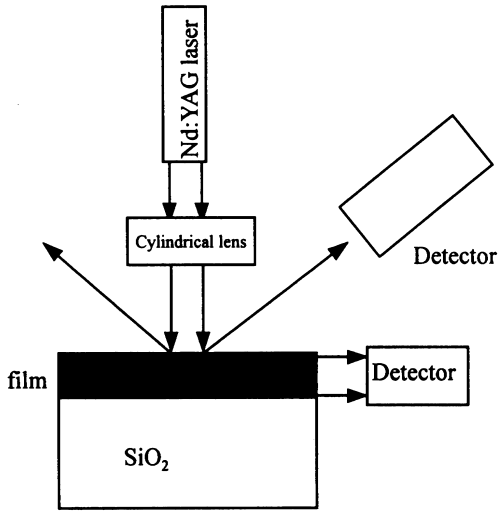

Fig. 1. The experiment schematic set-up.

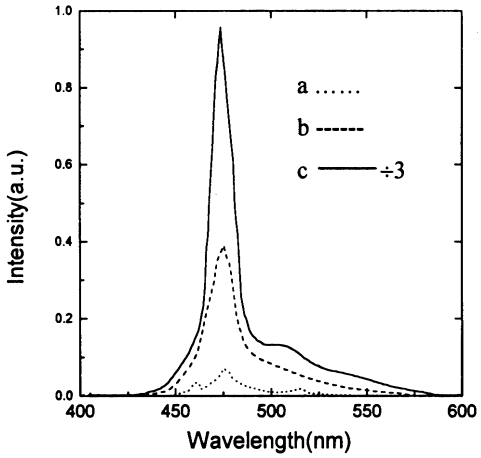

Fig. 3. The gain narrowing spectra detected from the side of the film of PS/perylene at different excitation pulse energy: (a) 1.6, (b) 4 and (c) 15 μJ.

which are located at 446, 476 and 506 nm, respectively. The main peak is at 446 nm. The similarity of the two spectra indicates that the luminescence of the perylene/PS film results from the emission of the perylene molecules. The function of the PS is to separate spatially the perylene molecules.

The changes of the emission spectra of the perylene/PS film at different pulses energies were illustrated in Fig. 3. Compared with the spontaneous emission spectrum shown in Fig. 2, the peak at 475 nm (curve (a)) became dominant at pump pulse energy of 1.6 μJ. Observed from the sides of the sample, there was a bright dot at the pump stripe end, which didn't exist at low excitation energy. The spectra showed a dramatic narrowing at pump pulses energy above this energy. The changes of the spectra detected at different pump energies indicated that the excitation threshold of gain narrowing was about 1.6 μJ. At excitation pulse energy of 15 μJ, the spectrum was narrowed with the peak at 475 nm, the FWHM of which was only 14 nm. It was also shown that when the gain narrowing occurred the peak at 446 nm in the original fluorescence spectrum was suppressed completely and the peak at 506 nm partly. The ASE peak was at 475 nm instead of 446 nm, which was stronger in the fluorescence spectrum. This was because the blend film showed a strong self-absorption near 446 nm.

It was believed that the gain narrowing spectra illustrated in Fig. 3 were due to the amplified spontaneous emission (ASE) guided in the blend film. The refractive indices of the substrate, the air and the film are 1.46, 1 and about 1.57, respectively. The refractive index of the film is greater than that of the surrounding media, so substrate/film/air actually constitutes an asymmetric planar waveguide. The emission light in accordance with waveguide modes can propagate in the film. During this process population inversion in the excitation area can be achieved if the pump pulses energy is high enough, then the spontaneous emission will be amplified along the stripe gain area. Consequently the spectrum will be enhanced and narrowed at the SE wavelength. If the thickness of the wave-guide layer was too thin, a

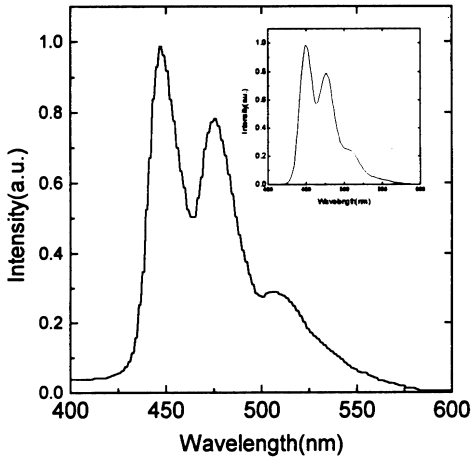

Fig. 2. The fluorescence spectrum of the blend film of perylene/PS. Inset was the fluorescence spectrum of the solution of perylene and THF.

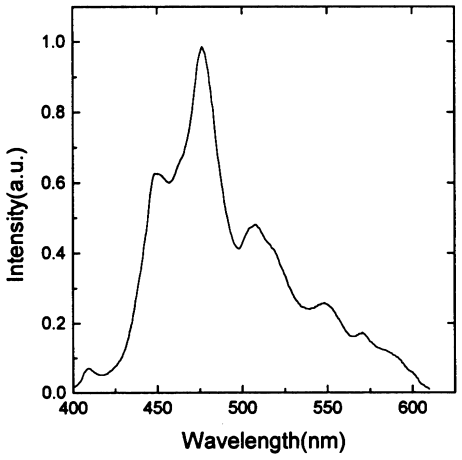

Fig. 4. The emission spectrum from the surface of the perylene/PS blend film when the excitation pulse is 15 μJ.

fundamental mode will not be supported, which means that there exists a cut-off thickness for the mode guide. According to the refractive indices of the air, the substrate and the film, the cut-off thickness of the first order mode was calculated. It is approximately 500 nm. In this study the thickness of the films was controlled for about 600 nm.

The spectrally gain narrowing was observed only in the parallel direction of the film. Fig. 4 shows the emission spectrum of the perylene/PS film detected from the film surface at excitation pulse energy of 15 μJ. The spectrum still exhibited the spontaneous properties. This was because that the light wave refracted out of the surface of the film remained mainly the spontaneous emission. This confirmed that the gain narrowing phenomenon shown in Fig. 3 was due to the waveguided ASE in the film. Note that in the spectrum there was still a stronger peak at 475 nm, as was different from that detected at low energy. It was believed that this was due to the imperfection inside the film and on the film surface resulted in scattering. Thus a little part of the SE was received when detecting the emission from the perpendicular direction of the film surface. When the ASE occurred we could see the excitation stripe extended at the two sides, which was another proof that scattering occurred.

4. Conclusion

The optically pumped ASE phenomenon in the substrate/film/air wave-guide structure was demonstrated. The active medium was the blend film of perylene/PS. At low excitation pulses energy the spectra showed dramatic gain narrowing in the submicrometer-thick film.

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