Solvent-vapour treatment induced performance enhancement of amplified spontaneous emission based on poly[2-methoxy-5-(2′-ethyl-hexyloxy)-1, 4-phenylene vinylene]*

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In this work, performance enhancements of amplified spontaneous emission (ASE) from poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) have been achieved via solvent vapour treatment. Correlations between the morphology of the film and the optical performance of polymer-based ASE are investigated. The active layers are characterised by atomic force microscopy and optical absorption. The results show that the solvent-vapour treatment can induce the MEH-PPV self-organisation into an ordered structure with a smooth surface, leading to enhanced optical gain. Thus the solvent-vapour treatment is a good method for improving the optical properties of the MEH-PPV.

Keywords: polymer semiconductor, amplified spontaneous emission, solvent-vapour treatment

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1. Introduction

Polymer semiconductors are attractive gain media for lasers and optical amplifiers due to their high photoluminescence quantum efficiencies, large stimulated emission cross-sections and chemically tunable emission wavelengths.[1−4] The demonstration of amplified spontaneous emission (ASE) in conjugated polymers also makes these materials promising as high gain media for cheap solid-state lasers and broadband optical amplifiers.[1−9] Considerable efforts have been made into improving the optical property by various treatments, such as application of electric field,[10,11,12] choice of solvent,[13] thermal annealing [14] and solvent vapour treatment.[15−18] The solvent vapour treatment can influence the characters of optical absorption and the charge carrier transport. Zhao *et al.* reported that 1,2-dichlorobenzene (DCB) vapour treatment can induce P3HT self-organization into an ordered structure, leading to enhanced absorption and a high hole mobility.[15]

Among the conjugated polymers, the family of poly (phenylene vinylene) has attracted considerable attention due to its interesting optical and electrical properties.[2,3] Poly[2-methoxy-5-(2′-ethylhexyloxy)-1,4-phenylene vinylene] (MEH-PPV), the first soluble PPV, has proved to be very attractive and applications such as lasers, OLEDs, photovoltaic cells and field effect transistors have been realized.[3,8,9,11] In this work, we report the ASE from MEH-PPV films treated by solvent vapour and discuss its relation to the surface morphology. This study reveals that the solvent vapour treatment can induce the MEH-PPV self-organization into an ordered structure with a smooth surface, leading to a decrease in the threshold of ASE and an enhancement of ASE optical gain.

2. Experiment

In our experiment, the planar thin films were fabricated by spin coating of toluene solutions of MEH-PPV onto cleaned glass substrates. The MEH-PPV

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solution concentration was 7 mg/ml. The MEH-PPV films were 120 nm thick, measured by an Ambios Technology XP-2 surface profilometer. Subsequently, the samples were transferred into a sealed container filled with organic solvent vapour and held for 30 min. Finally, the devices were dried at 70 °C for 1 h in a vacuum chamber.

The samples were optically pumped at 500 nm by an optical parametric oscillator (OPO), the latter was pumped by a Q-switched neodymium ion-doped yttrium aluminum garnate (Nd^{3+}: YAG) laser. A schematic diagram of the setup for ASE measurements is shown in Fig. 1(a). The OPO delivered 5 ns pulses at a repetition rate of 10 Hz. The pulse energy incident on the sample was adjusted by the insertion of neutral density filters into the beam path. A narrow excitation stripe of about 0.5 mm × 3 mm was focused on the sample with an adjustable slit and a cylindrical lens. 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.[8] The UV/V absorption spectra were measured on a UV-3101 PC UV–VIS–NIR scanning spectrophotometer. The atomic force microscopy (AFM) images were taken with Digital Instrument Nanoscope IIIa.

3. Results and discussion

Figure 1(b) shows the absorption, the photo luminescence (PL) and the ASE of the MEH-PPV film. The PL spectrum of the MEH-PPV thin films has a vibrational peak at 620 nm (0–1 transition) with another vibrational peak at 580 nm (0–0 transition). Above the threshold energy density for the ASE, ∼0.2 μJ/pulse, the full width at half maximum (FWHM) is gradually narrowed and reaches a value of ∼10 nm with the increasing pump energy density. The narrowed spectrum is located at 620 nm, which is close to 0–1 vibrational peak, where the net gain is the highest. The mechanism of this spectral narrowing has been attributed to the ASE.[2,8]

The output emission intensities of samples as a function of the pump intensity are shown in Fig. 2. It can be seen that the treated layers affect the emission spectra of the MEH-PPV film strongly. Obviously, when the films are treated by the organic solvent vapour, a stronger ASE peak is observed. To investigate the influence of different solvent vapour treatments on the ASE, we compare the thresholds and the gains of the MEH-PPV films treated in different solvent vapours. The emission intensities increase slowly with the increase of the pump intensity for the untreated films, as shown in Fig. 2. The treated films show first a rise in the slope, followed by a linear increase in the output signal as the excitation energy is increased. Therefore, the thresholds of the pump energy for the ASE can be calculated to be 219.3, 192.6 and 179.6 μJ/pulse corresponding to the pristine MEH-PPV films and the MEH-PPV films treated by toluene vapour and by chloroform vapour, respectively. It is found that the thresholds of the MEH-PPV films treaded by toluene and chloroform vapours decrease to 87.8% and 81.9%, respectively.

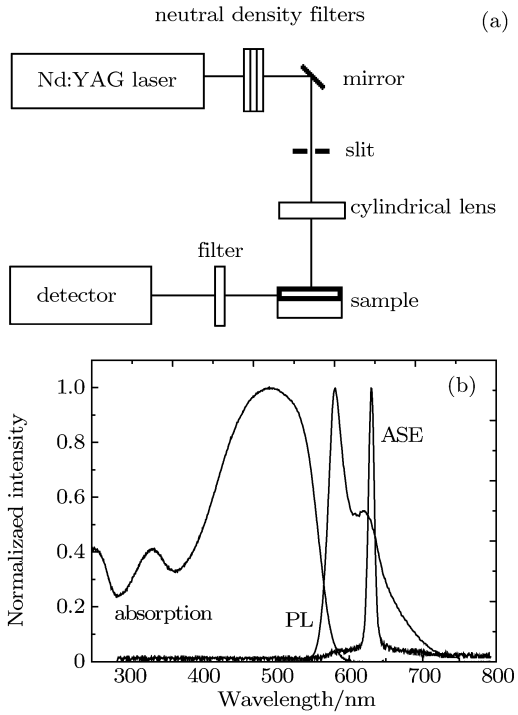


Fig. 1. (a) Schematic diagram of the setup for the measurement of ASE. (b) Normalised MEH-PPV thin-film absorption, photoluminescence (PL) and ASE spectra.

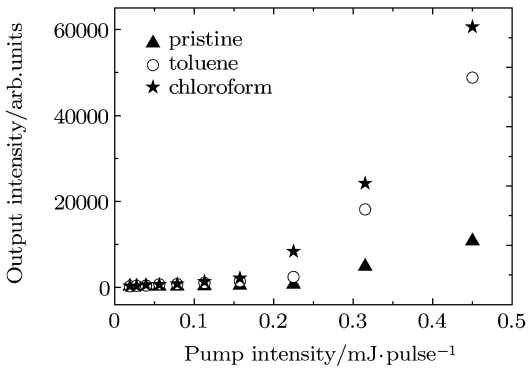


Fig. 2. Output intensities of MEH-PPV films treated in different solvent vapours as a function of pump energy.

In order to demonstrate the ASE and the lasing characteristics of the MEH-PPV films, the gain characteristics of waveguides are also studied in detail.

The net gain is measured by using the usual variable-stripe-length (VSL) method, which has been widely used to characterize the gain in organic semiconductor slab structures. For the case of ASE, the output intensity is given by the following expression[2,3]

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

where $A(\lambda)$ is a constant related to the cross section for the spontaneous emission, $I_{\rm p}$ is the pump intensity, $g(\lambda)$ is the net gain coefficient and L is the length of the pumped stripe. Figure 3 shows the dependence of the output intensity on the excitation stripe length at the pump energy of 0.3 μJ/pulse. The solid curves in Fig. 3 are the fits of the experimental data according to Eq. (1), having net gains of 15.5, 21.0 and 21.7 cm^{-1} at the pump energy of 0.3 μJ/pulse. This indicates that slow-solvent-vapour treatment can increase MEH-PPV ASE characteristics. The performances of these devices are summarized in Table 1. The devices with the active layers of MEH-PPV treated in solvent vapour behave better than those with pristine active layers.

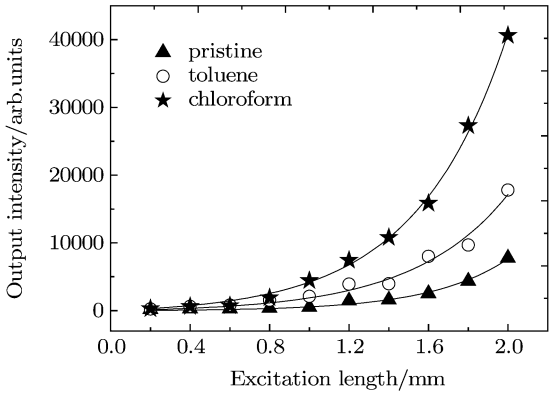


Fig. 3. The dependence of the emission intensity on the excitation length for the samples treated in different solvent vapours at the pump intensity of 0.3 μJ/pulse.

Table 1. Amplified spontaneous emission characteristics of the active layers treated in different solvent vapours at the pump energy of 0.3 μJ/pulse.

	Peak /nm	$I_{\rm th}$ /nJ·pulse^{-1}	Gain /cm^{-1}	Roughness /nm
Pristine	620	219.3	15.5	0.80
Toluene	620	192.6	21.0	0.43
Chloroform	619	179.6	21.7	0.40

In order to further elucidate the effects of solvent vapour treatment on the morphology of the MEH-PPV film, the microstructures of the MEH-PPV films are studied via measuring absorption spectra and taking AFM images.

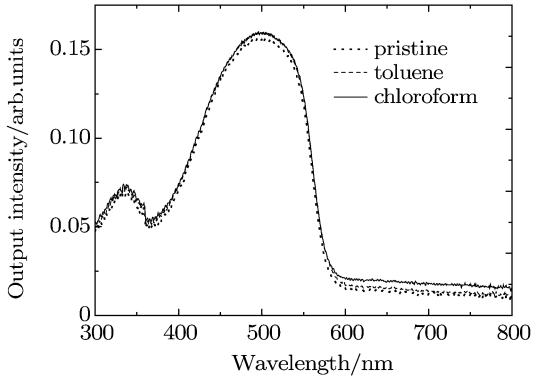


Fig. 4. Absorption spectra of the MEH-PPV films treated in different solvent vapours.

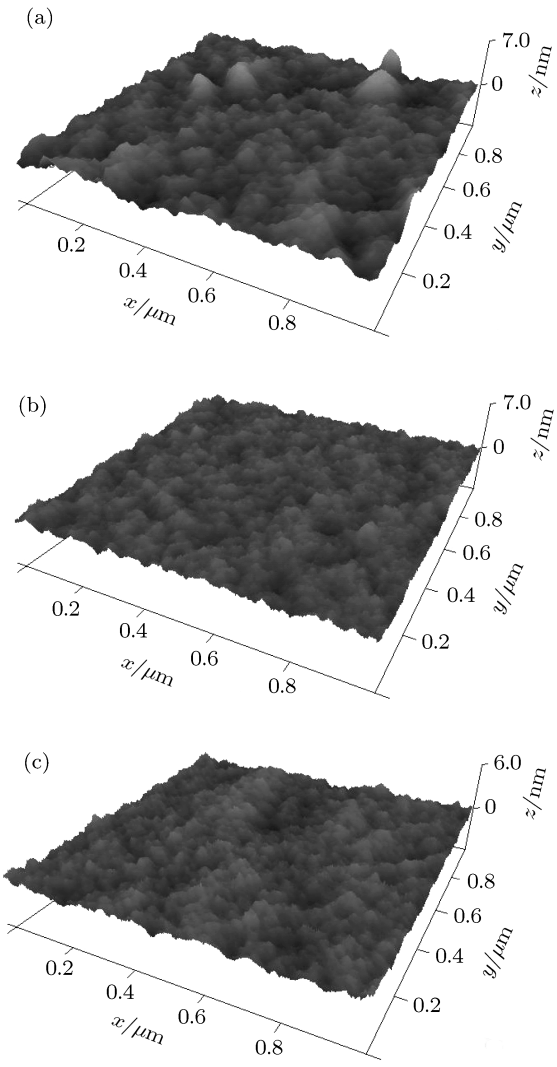


Fig. 5. AFM height images of (a) as-spun MEH-PPV film, (b) toluene-vapour treated one and (c) chloroform-vapour treated one.

The different absorptions of the MEH-PPV films due to different treatments are shown in Fig. 4. For

the untreated and treated films, the MEH-PPV absorption peaks are all located at 500 nm. Compared with the untreated film, the absorptions of solvent vapour treated films become unconspicuously stronger. The enhanced absorption via solvent vapour treatment has been reported in other papers.[15,18] However, a little enhancement in optical absorption cannot testify the enhancement of ASE.

Figure 5 shows the AFM height images of the MEH-PPV films with different solvent-vapour treatments. For the as-spun film (a), a surface with a root-mean-square (RMS) roughness of 0.80 nm is observed. The films treated with toluene (b) and chloroform (c) vapours are much smoother than the as-spun film, showing RMS roughness of 0.43 and 0.40 nm in the 1 μm $\times$ 1 μm scan area, respectively. This is because the MEH-PPV chains self-assemble into an ordered structure and the roughness decreases after the toluene and the chloroform vapour treatments. Because the volatility of chloroform is larger than that of toluene, the concentration in the chloroform container is larger. Thus, the film treated by the chloroform vapour is smoother than that treated by the toluene vapour. The smooth surface can increase total reflection and decrease the light propagation loss. Then, it can result in the enhancement of the gain of the ASE device. It can be demonstrated that the smoothness induced by the slow-solvent-vapour treatment controls the nanoscale organizations of MEH-PPV molecules in the photoactive layers and induces performance enhancement of the ASE.

4. Conclusion

The performance of the amplified spontaneous emission from poly[2-methoxy-5-(2′-ethyl-hexyloxy)-1,4-phenylene vinylene] can be obviously enhanced by the solvent vapour treatment. An improved film morphology and a self-assembled MEH-PPV are obtained. Different solvent vapours can induce different morphologies of the MEH-PPV films, directly influencing the performances of the devices. The solvent-vapour treatment is a good approach to improve the optical properties of the MEH-PPV.

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