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Optical and Electrical Properties of Poly(3-alkylthiophene) and Laser Emission from Microcapillary Geometry

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The conducting polymers, which have linear pattern of alternating single and double bonds in their main chain, exhibit semiconducting properties [1], and a lot of them are capable of light emission. This can be generated either optically or electrically; the latter process is very promising as polymer light-emitting diode [2]. In addition, their charge carrier transport properties also lead to the realization of the future devices such as solar cells [3] and transistor [4]. Most polymer devices can be fabricated by the wet process such as spin-coating, casting and ink-jet printing. These outstanding characteristics cause the low-cost mass production of simple fabrication process.

Recently, intense studies of the polymer laser deveices have been achieved. There are several reasons why the conducting polymers could be attractive laser materials [5]. The first is that light across the visible spectrum can be emitted from various polymers. They have broad spectra, providing possibility for the tunable lasers. The absorption and photoluminescence spectra are well separated, so that absorption of emitted light is weak. Conducting polymers also can emit intense light as neat solid films, are capable of charge transport, thereby providing the potential to make electrically pumped lasers in the future.

Poly(3-alkylthiophene) which has the excellent conductivity has been widely studied as the devices, such as photovoltaic cells [3]. Besides, PAT also are implied the different electrical and optical properties derived from the side-chain structure, such as regio-random and regio-regular, have been investigated within the framework of the basic science and applications. The low mobilities of conducting polymers limit the current densities in polymer devices, so that the excitation densities required for laser operation are hardly achieved. It is, therefore, desirable to understand and improve the optical design of the polymer lasers which exhibit the high carrier mobility.

In this study, we report on lasing from high quality thin film of PAT in microcapillary structure.

We used regio-random poly (3-dodecylthiophene) (PAT12) as the laser medium. The microcapillaries with the inner diameters of 75 μm were dipped into the chloroform solution of PAT12, and the polymer neat films were deposited onto the inside surface of the microcapillaries with capillary action spontaneously. These microcavities have the excellent potential as future laser devices, because of the simple and low-cost fabrication techniques utilizing the solution process of the conducting polymers.

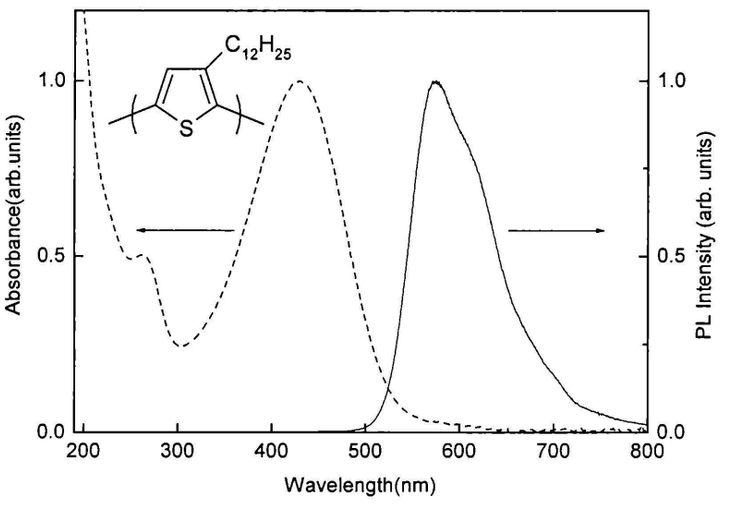

Fig. 1. Absorption and PL spectra of PAT12 thin films. The inset is the molecular structure of PAT12.

For the PL measurements at high excitation intensities, we used a Nd: yttrium aluminum garnet (YAG) regenerative laser amplifier producing 100 ps pulses with a repetition rate of 1 kHz. This laser light was frequency tripled (355nm). The pump laser beam was focused by a round lens onto the samples with the polymer films and the emission was detected by a spectrometer and a charge-coupled device array from the side at perpendicular to the direction of the pumping beam. The samples were held in a vacuum cell to avoid the degradation by irradiation and oxidation.

Figure 1 shows the absorption and photoluminescence (PL) spectra of PAT12 thin films, and the insets show the molecular structure of PAT12. The peak wavelengths were 430 nm for absorption and 575nm for PL, respectively. These spectra were well separated, so that absorption of emitted light is weak. In many fluorescent organic molecules, light emission is severely quenched at high concentrations. It implies that there is the potential for strong amplification of light. PAT12 can emit light as neat solid films and are capable of charge transport as laser materials.

The emission spectrum of the PAT12 thin film with the microcapillary structure was shown in the Fig. 2 (a), and the insets show the schematic cross section of microcapillary structure. We observed the sharp lines in this spectrum with a constant mode spacing. The threshold pump energy is approximately 4.9 nJ/pulse, as shown in the Fig. 2 (b).

To explain the emission lines more precisely, we use positive harmonics in the Fourier transform of the emission spectrum. The Fourier transform gives the product of the effective index of refraction, n, and cavity diameter, D and contains a number of sharp peaks located at the length of a multiple of $nD/2$ with the circular geometry [6][7].

In this case, Bessel functions describe the field intensity in cylindrical microcavities, and thereby an integer Bessel function corresponds to each emission line. The argument of the integer Bessel

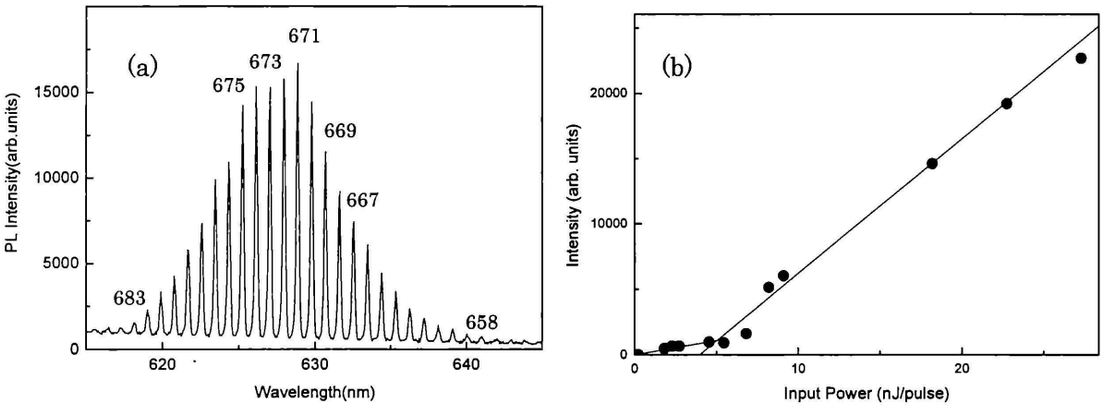

Fig. 2. (a) The emission spectrum of PAT12 in microcapillary structure and the inset is schematic image of a cross-sectional view of the micro capillary structure. The integer beside the spectral line means correspondent Bessel function s. (b) Emission intensity as a function of excitation.

function, $J_s(kr)$ must be zero at the polymer/air interface assuming the field to be zero at the interface:[6]

$$J_s\left(\frac{\pi nD}{\lambda}\right)=0 \tag{1}$$

Bessel functions have many zeros, so this condition can be written as

$$X_{st}=\left(\frac{\pi nD}{\lambda}\right) \tag{2}$$

where X_{st} is the tth zero of Bessel function of order s. Figure 3 is the Fourier transform of the emission spectrum in Fig. 2 (a). The units of the Fourier transform are length if we measure in wave vector ($k = 2\pi/\lambda$) as the units of the emission spectrum. This spectrum has several well-spaced peaks. The effective index of refraction was estimated 1.85 with the microring diameter $D = 75$ μm and $nD = 137.63\mu$m.

The largest peak in the emission spectrum of Fig. 2 (a) is at $\lambda = 628.9$ nm, the first zero of Bessel function occurs at 688 and it is calculated 704.50. The estimated wavelength λ with eq. 2 is figured 613.7 nm in disagreement with the experimental spectrum. The investigation of Bessel functions with the first zero at the polymer/air interface near s reveals $s = 671$, and the first zero of Bessel function for this value is 687.36. It means an expected wavelength of $\lambda =$

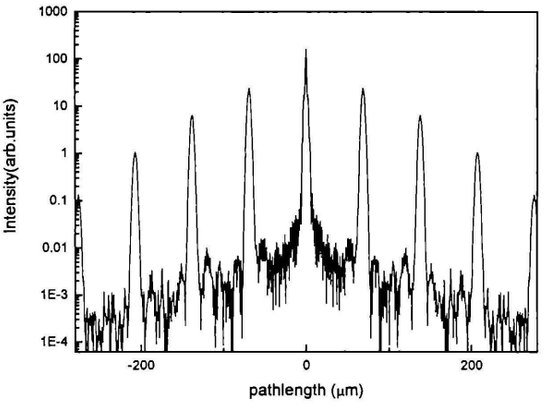

Fig. 3. Fourier transform of the emission from PAT12 on the inside surface of the microcapillary in Fig.2 (a)

629.0 nm, which corresponded to 628.9 nm from the experimental measured value. Contiguous emission peaks correspond to successive integer values of Bessel functions. All series of emission peaks are fitted with a series of Bessel functions $658 < s < 683$ correspond with 618-641 nm as shown in Fig. 2 (a).

In conclusion, we observed the laser emission of PAT12 from the microcapillary structures. Each set of multi-mode laser emission peaks is described by the cavity length from the Fourier transform, and a series of integers for s. The microcapillary structures were superior to the conventional microring because of the high quality polymer thin film fabricated by spontaneous capillary action. These cavities could be candidates for the polymer laser structures pumped by the microchip such as inorganic or polymer LEDs as compact, low-cost tunable sources, and lead to the polymer laser diodes by direct current injection in the future.

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