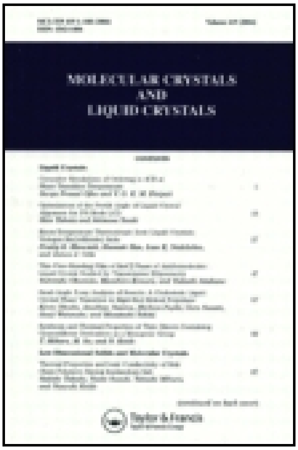

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Akihiro Tomioka [a], Yasushi Kamiyama [a], Yoshiyuki Ohno [a], Kota Otani [a] & Yuki Kosuge [a]

[a] Graduate School of Engineering, Osaka Electro-Communication University, Osaka, Japan

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Amplified Spontaneous Emissions from π-Conjugated Polymer Film: Modulation by Evanescent-Field in a 1-D Photonic Crystal Substrate

Akihiro Tomioka, Yasushi Kamiyama, Yoshiyuki Ohno, Kota Otani, and Yuki Kosuge
Graduate School of Engineering, Osaka Electro-Communication University, Osaka, Japan

One-dimensional photonic crystal (PC) with alternating layers of TiO_2 *and* SiO_2 *was fabricated with spin coating and low temperature baking, resulting in a successful tuning of the PC stop band so as to block the amplified spontaneous emission (ASE) from a π-conjugated polymer film. Single PC as a substrate, not a cavity with two PC's, of the polymer film was sufficient to shift the tangential ASE to the energy at PC stop band edge, indicating that the tangential ASE propagating along the interface was modulated by its evanescent-field tail in the PC, which opens a possibility for wide tuning of the coherent luminescence from an ultrathin π-conjugated polymer film with ultimate mode volume.*

Keywords: π-conjugated polymer; amplified spontaneous emission; evanescent field; photonic crystal; vibrational mode

INTRODUCTION

Conjugated polymers offer promise as both electrical and optical materials with their versatility and flexibility [1]. Application to incoherent organic light emitting devices being already in steady progress, an application to coherent light source becomes a new challenge [2]. To fabricate a device structure, solution process in the ambient atmosphere is a promising process [3]: it is promising in view of the process

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Address correspondence to Akihiro Tomioka, Osaka Electro-Communication University, 18-8 Hatucho, Neyagawa, Osaka 572-8530, Japan. E-mail: tomioka@isc.osakac.ac.jp

rapidity and the cost effectiveness without the need for high vacuum or high level of cleanness.

In the present study we fabricated one-dimensional (1-D) photonic crystal (PC) structures as a periodic repeat of two types of transparent layers with different indices of refraction, TiO_2 ($n = 2.4$) and SiO_2 ($n = 1.5$), using both spin coating and sol-gel reaction [4,5]. We discuss on a possible modulation of the optical gain dispersion among different vibronic transitions of a conductive organic dye film that is placed on the 1-D PC with a stop band covering the original amplified spontaneous emission (ASE) energy of the dye film, even when the tangential ASE propagates along the surface of the PC.

MATERIALS AND METHODS

The thickness of the TiO_2 layer was tuned by varying the concentration of the TiO_2 precursor ethoxide solution [4,5] in 2-propanol. The resulting TiO_2 layer was uniform and smooth only when spin coated from precursor solution with concentrations less than 4.5 mg/ml. When thicker TiO_2 layer was needed, TiO_2 layer was deposited several times (designated as "m" in Fig. 1(a)) successively to render the thickness m-times. We need a baking after each TiO_2 deposition because, without an intervening baking, the spin coated precursor film would be redissolved in the solvent of the next spin coating. Intervening SiO_2 layer was also made by spin coating precursor ethoxide solution, followed by baking on a plate heater.

The π-conjugated polymer, poly[2-methoxy-5-(2′-ethyl-hexyloxy)-*p*-phenylene-vinylene] (MEH-PPV), was used for an optical gain medium [6]: it is a chemically modified polymer of highly fluorescent PPV so as to achieve solubility in organic solvents for spin coating. The MEH-PPV was spin coated on a hydrophilic substrate surface after ozone treatment of the surface. To estimate the MEH-PPV film thickness, it was deposited on an ideally flat Si wafer with an ozone-treated natural SiO_2 layer atop, detached partially by a sticky tape to expose a film edge, and the surface profile was measured by an α-profilometer (Ambios XP-1).

To observe an ASE from MEH-PPV on a glass substrate, or on a PC, the excitation laser was tuned to the absorption maximum, 500 nm, outside of the PC stop band, and therefore can penetrate through the PC: the excitation was made by an optical parametric oscillator laser (OPOTEK Opolette 355 II, variable wavelength, 5 ns, 2 mJ/pulse at 20 Hz repetition rate, reduced to 15 μJ/pulse by ND filters) focused by an $f = 8$ mm cylindrical lens to shape the beam

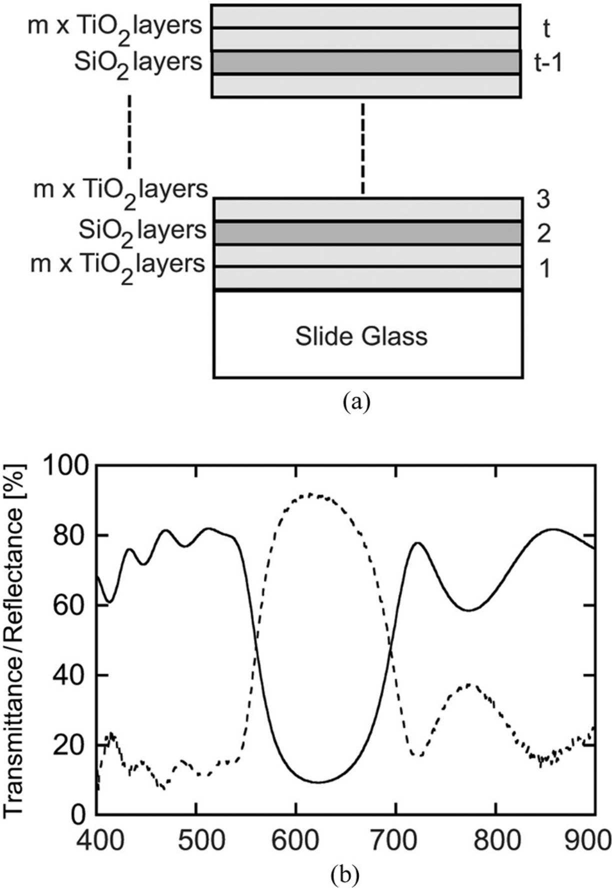


FIGURE 1 (a) Schematic drawing depicting the one-dimensional PC structure composed of alternating layers of TiO_2 and SiO_2 glasses on top of a slide glass. (b) The transmittance (solid curve) and reflectance (broken curve) spectra of a typical 1-D TiO_2/SiO_2 PC.

into a rectangle. The specimens were sealed in a nitrogen-filled custom-made chamber with three faces covered by glass window to avoid possible dye degradation [7]. Photoluminescence (PL) or ASE from the specimen was collected by an objective, passed through a dichroic filter to reject the scattered excitation laser, and was coupled to a spectrometer (resolution: 1.6 nm). The PL spectrum was recorded by a back-illuminated CCD camera cooled down to $-70°C$ by Peltier elements with on-chip multiplication capability (Princeton Instruments, PhotonMAX 97EMB).

RESULTS

Fabrication of 1-D PC

Typical optical transmittance and reflectance spectrum of the resultant PC ($m = 4$ and $t = 7$) is shown in Fig. 1(b), demonstrating a successful formation of stop band (reflectance >0.9) from 560 nm through 680 nm where the light does not penetrate through the PC, leaving high transmittance regions below 550 nm and above 700 nm.

Solution process to fabricate 1-D PC's is a rapid and convenient process compared to more elaborate vacuum deposition processes: a group of 4 identical PC's of Figure 1(b), made by 19 spin coating and 19 baking, needed only 3 hours to fabricate. It takes only a few seconds for spin coating, whereas subsequent baking is time-consuming and may generally need 10 minutes. Although most precursor manufacturers recommend the TiO_2 baking at 450°C, we succeeded in baking at lower temperature 300°C and only for 2 minutes to reduce the processing time and the energy of heating: the resulting PC's showed a negligible optical change for two weeks. We adopted therefore this baking condition throughout the present study, which enabled us to manufacture PC's in ten minutes per each repeat of the periodic structure.

When the effective concentration, that was defined by the actual concentration multiplied by the number m of multiple depositions, of TiO_2 precursor solution was varied from 80% to 250%, the longer wavelength edge of the stop band was modified linearly. This index, the effective concentration, provides a reliable practical measure for the layer thickness to tune the PC stop band because the identical effective concentration yielded similar stop bands, even for different numbers of depositions.

ASE of Polymer Film on a Glass Substrate

A thin film of a conductive π-conjugated polymer, MEH-PPV, was spin coated, first on a glass substrate, to evaluate the wavelength of inherent ASE [7]: the ASE was observed at a peak of 615 nm with FWHM (full width at half maximum) of 10 nm (thin curve in Fig. 2) when the excitation power was just above a threshold of 3 $\mu J/mm^2$. This ASE peak seems to correspond to the 0–1 vibronic transition of MEH-PPV that is seen as a shoulder in the absorption spectrum, suggesting that efficient ASE was attained as the transition from an excited state down to the low populated first vibronic state of the ground level (Fig. 3). The excitation threshold was much lower than that of a monomer dye film, where a mode selection was achieved

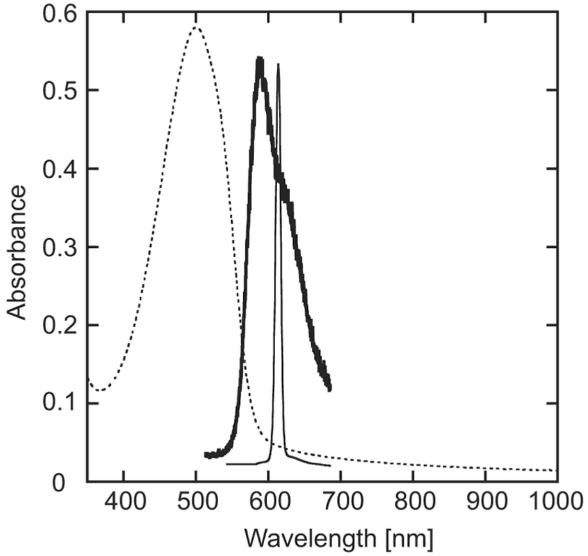


FIGURE 2 Absorption spectrum (dotted curve), PL spectrum (thick curve), and ASE spectrum (thin curve) of the MEH-PPV film.

owing to a possible dye ordering due to capillary force at the air-solution boundary during the film deposition [8].

The ASE peak height was proportional to the excitation power subtracted by the threshold value, and the peak linewidth decreased

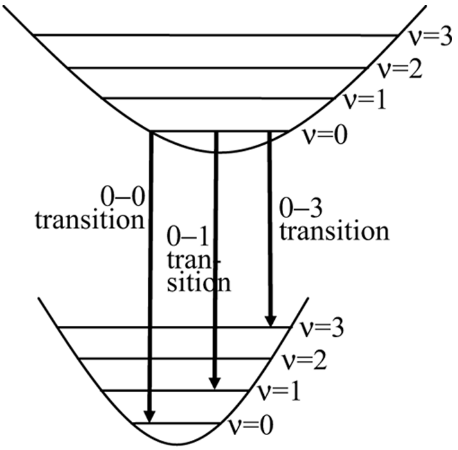


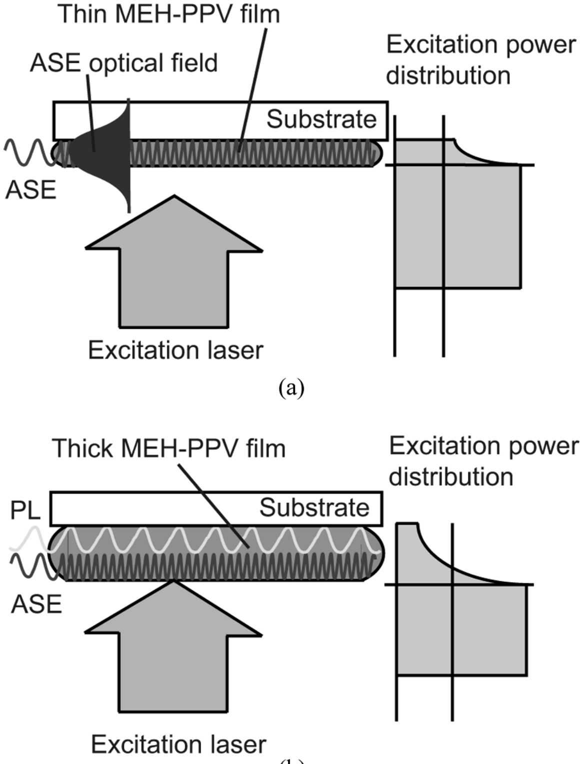
FIGURE 3 Schematic model of vibronic transitions of MEH-PPV dyes.

ideally at the same threshold, when the polymer film was spin coated from a 15 mg/ml MEH-PPV solution. In contrast, thinner films spin coated from lower concentration solution showed nonuniform thickness judging from the position-dependent absorption, and did not show ASE even at 120 μJ/mm^2 excitation power: a dewetting process [9] may hinder the uniformity of the film below 15 mg/ml. We adopted an ozone treatment prior to spin coating so as to render the substrate surface hydrophilic because the treatment practically brought about better uniformity of the film, in spite of the hydrophobic nature of MEH-PPV. A uniform film of thinner MEH-PPV on a substrate with better surface treatment may realize a lower threshold ASE. Better uniformity is expected when the MEH-PPV film is spin coated on an ideally flat Si-wafer with naturally-grown SiO_2 layer on top: contrary, no ASE was attained actually even at the 120 μJ/mm^2 excitation power, due to a reduced excitation field by the reflected excitation laser at Si surface. This observation is consistent with other reports [10] which described that the film thickness of ca. ASE wavelength was necessary for ASE observation when a Si wafer was used as a substrate. When the polymer film was spin coated from a 19 mg/ml solution to form a thicker film, ASE peak coexisted with a broad PL profile, even at excitations over a threshold: the excitation power should decrease across the film thickness in this thick film (Fig. 4). Around the threshold, the forefront part of the film is expected to be excited enough to reach an ASE, whereas the backside got a weaker, insufficient excitation, staying at incoherent PL regime.

The thickness of the MEH-PPV film made from 15 mg/ml solution was estimated as 85 nm based on the measurement with α-profilometer. Since the thickness is less than 1/3 of the half wavelength of the observed ASE, the propagating ASE field cannot be confined inside the polymer film but is expected to extend out into the PC, and is therefore expected to be under the influence of the substrate optical property which is the topic of the next section.

ASE of Polymer Film on a 1-D PC

When a MEH-PPV film was spin coated upon the PC with a stop band from 560 to 680 nm, the intensity of the 615 nm ASE was lowered to a half, and a new ASE appeared at 680 nm, the lower energy edge of the PC stop band (solid curve in Fig. 5). The new ASE at 680 nm may correspond to the 0–3 vibronic transition of MEH-PPV which was selected as the energy near the stop band edge (Fig. 3). Selection of the vibronic transition other than 0–1 may be realized by an unharmonic oscillation of the real dye molecule. Further PC's with sharp stop band edge at



(a)

(b)

FIGURE 4 Schematic drawing (a) depicting a uniform excitation above the ASE threshold that was attained in the case of thin MEH-PPV film, and (b) depicting a nonuniform and insufficient excitation across the film depth in the case of thick MEH-PPV film, which leads to a coexistence of ASE and PL.

different energies are needed to demonstrate whether the modulated ASE energy would shift to one of the MEH-PPV vibronic transitions only when that vibronic transition energy is coincide with the PC stop band edge. Further discussion remains whether the linewidth could be narrower, determined by the steepness of the PC stop band edge. The remnant original ASE seems to shift to higher energy, away from the center of the stop band, possibly by a coupling with new ASE mode, which should be checked by modulation with PC's with different stop band edge. The light which penetrated through the PC did not show any ASE even at $120\,\mu J/mm^2$ excitation power: ASE at 615 nm was prohibited by the PC stop band and the film thickness was insufficient as a cavity length for ASE to grow at 680 nm.

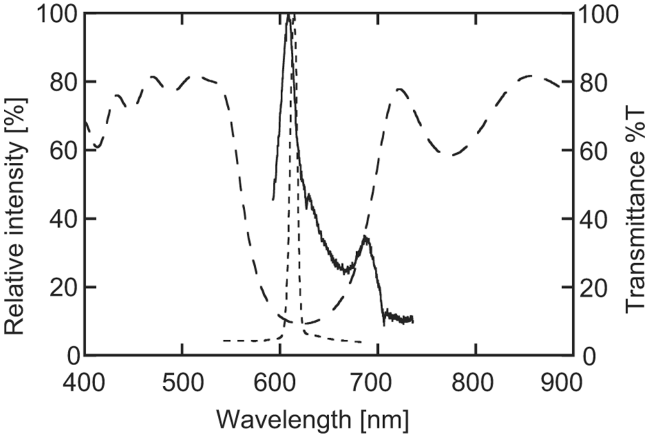


FIGURE 5 Comparison between the ASE of a MEH-PPV film on a TiO_2/SiO_2 PC (solid curve) and that of the same thickness MEH-PPV film on a glass substrate (dotted curve). The transmittance spectrum of the underlying PC is shown by a broken curve.

The observed ASE was in the direction along the polymer film and it did not penetrate through the PC: nevertheless the result of Figure 5 shows that the PC stop band dispersion determined the ASE wavelength. This observation suggests that the ASE mode propagating at the PC-dye film interface carries evanescent field inside the PC (Fig. 4(a)) which rejected the original ASE energy within the PC stop band photon energy, accepting a new ASE at the stop band edge. Improvement to higher rejection of the original ASE energy may be accomplished by a perfect stop band of a PC with sufficient number of repeats.

A prior surface treatment of the substrate PC so as to lower the surface energy of the MEH-PPV solution would also be helpful: a thinner uniform waveguide on the PC would convey an evanescent field as a major component, possibly leading to a perfect ASE modulation in this mechanism, as well as showing a lower ASE threshold as a result of small mode volume. Small mode volume is regarded as an essential factor for ultimate low threshold lasing [11] that is expected to conjugated organic materials with high oscillator strength. Present specimen, still lacking a sufficiently low threshold due to the waveguide bottom surface roughness, nevertheless demonstrated the effectiveness of the evanescent field as an ASE modulation driving force. Once a thin uniform waveguide is fabricated, modulation of coherent emission via evanescent-field may be preferable to control this small mode volume lasing system.

CONCLUSION

One-dimensional photonic crystal (PC) was fabricated with the use of a solution process and a baking at medium temperature of 300°C, indicating a clear stop band in the optical transmittance. A π-conjugated polymer thin film, formed on top of the PC with a stop band covering the polymer ASE energy, generated a new ASE at the stop band edge, suggesting that the evanescent tail of this surface propagating ASE modulated the ASE via the selection rule of the PC stop band.

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