Blue, surface-emitting, distributed feedback polyfluorene lasers

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We report the fabrication of optically-pumped solid-state distributed feedback lasers utilizing two blue-light-emitting semiconducting polyfluorenes as gain media. The lasers were readily fabricated by solution deposition of thin polymer films on top of gratings etched into fused silica substrates. A compact Nd:YVO_4 microchip laser was used as the pump source for the two polymers studied, and lasing was achieved at 455 and 465 nm. Low threshold energies, $\geqslant$4 nJ per pulse, were obtained. The emission characteristics of the lasers are described along with the results of additional experiments that investigate in more detail the effect of the grating microstructure on polymer light emission. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1612903]

Following encouraging reports of stimulated emission in semiconducting (conjugated) polymer films, increasing attention has recently been paid to their development as solid-state gain media for use in lasers and optical amplifiers.[1–3] Amplified spontaneous emission has now been observed in many conjugated polymers[3] and laser action has been achieved for a variety of resonator designs, including microcavity,[4] microring,[5] and distributed feedback grating structures.[6–10]

An important future target is the realization of an electrically-pumped solid-state polymer laser diode. For this purpose, high current densities must be achieved within the polymer layer in addition to the large net optical gain and low stimulated emission thresholds required for optical pumping. Fluorene-based polymers (polyfluorenes) have established themselves as a particularly attractive class of materials. They show excellent charge transport properties, high fluorescence quantum efficiencies, and exhibit high net gain across the entire visible spectrum.[11,12]

The polymers utilized here as gain media are two polyfluorenes, namely poly(9,9-dioctylfluorene) (PFO) and poly[9,9-dioctylfluorene-*co*-9,9-di(4-methoxyphenyl) fluorene] (F8DP). Both polymers show strong, low threshold stimulated emission in the blue spectral region and exhibit large net optical gain coupled with low loss in slab waveguide geometries.[12,13] While to date most conjugated polymer lasers have used large-frame, bulky laser systems for optical pumping, red lasing has recently been reported in a conjugated polymer laser that is pumped by a compact microchip laser.[14] In this letter, we demonstrate that such simple and compact systems can also be applied to generate light in the technologically important blue spectral region.

The lasers were made under clean room conditions by deposition of thin polymer layers on top of suitably corrugated fused silica substrates, to produce asymmetric slab waveguides that support only the fundamental transverse electric mode for the wavelengths of interest. A schematic representation of the laser structures is shown in Fig. 1(a). The substrate corrugations were defined holographically in photoresist layers on silica substrates. Subsequent development of the photoresist and reactive-ion etching into the silica substrates, formed the final grating structures which had a period Λ=288 nm and a depth of ~30 nm. Thin polymer films were then spin coated on top of the gratings from 20 mg/ml *p*-xylene (for PFO) or toluene (for F8DP) solutions, to form the active guiding layer for each laser. The polymer layer thickness was ~100 nm for the PFO and ~120 nm for the F8DP lasers.

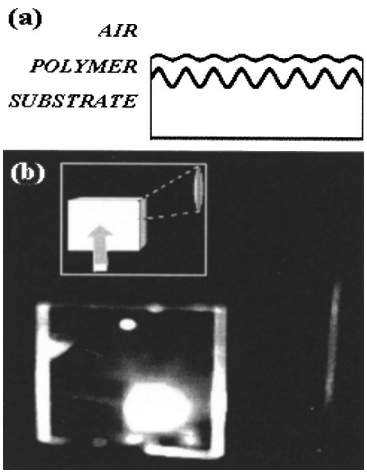

FIG. 1. (a) Schematic of the DFB laser structures and (b) photograph of a PFO DFB laser in operation. The pump beam is incident at ~20° and the DFB laser radiation is emitted in a fan perpendicular to the structure, as shown schematically in the inset.

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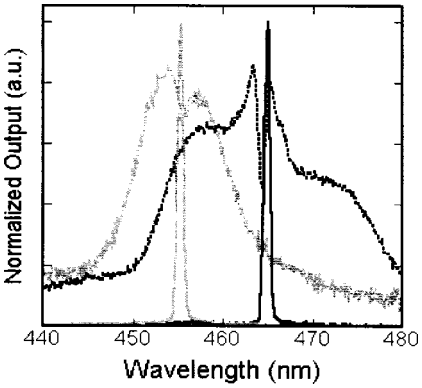

FIG. 2. Emission spectra of the PFO (gray lines) and F8DP (black lines) DFB lasers, taken below (dotted lines) and above (solid lines) the lasing threshold. (Note that the emission intensities have been arbitrarily scaled to allow direct comparison in a single plot.)

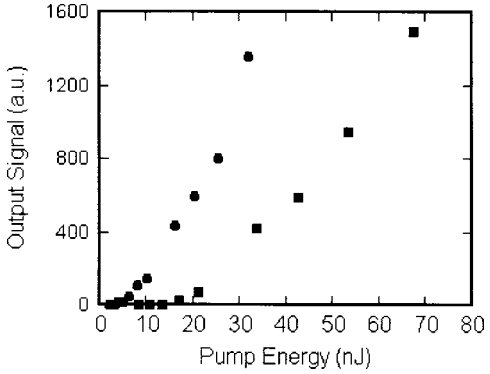

FIG. 3. Peak output intensity from the PFO (filled squares) and F8DP (filled circles) lasers as a function of the excitation pulse energy.

In our distributed feedback (DFB) lasers, optical feedback is provided through second-order Bragg scattering of the waveguided radiation. This is induced by the substrate corrugations and couples counterpropagating waves within the film plane.[15] Lasing occurs at a wavelength near $\lambda_{\text{Bragg}} = n_{\text{eff}}\Lambda$, where n_{eff} is the effective refractive index of the waveguide and Λ, the period of the grating. The latter was carefully chosen, so that feedback could be achieved at wavelengths within the gain region of both of our polymers. The laser beam is output coupled by first-order Bragg scattering, which supports radiation in a direction perpendicular to the substrate. For excitation we used a compact frequency-tripled Nd:YVO_4 microchip laser (having dimensions 40 $\times 40 \times 60$ mm^3), emitting $\sim$1 ns pulses at 355 nm. The pump beam was incident upon the structures at $\sim 20°$ and formed a rectangular spot of dimensions 250 μm$\times$100 μm. The emitted radiation was collected normal to the surface using a fiber-coupled spectrograph equipped with a charge coupled device detector.

Figure 1(b) shows an image of the far field transverse emission pattern of the PFO/DFB laser at a pump energy above the lasing threshold. The emission pattern is ''fan'' shaped, as expected for a one-dimensional DFB resonator.[6,7] The emission perpendicular to the grating axis is highly confined, while that parallel to the grating axis (along which the emission is polarized) has higher divergence. We note, however, that two-dimensionally, nearly diffraction limited emission can be achieved with a suitable two-dimensional DFB structure.[9,10]

Figure 2 shows the emission spectra of the PFO and F8DP lasers measured for emission parallel to the substrate normal, for excitation energies above and below their respective lasing thresholds. For pump energies below threshold, the output spectra consist of the normal low intensity, broad, polymer photoluminescence (PL) modified by sharp peaks corresponding to waveguided PL which has been Bragg scattered out of the waveguide at an angle normal to the substrate ($\varphi = 0°$). These spectra exhibit a characteristic dip in emission intensity due to an inhibition of the propagation of waveguided PL photons by the grating. This Bragg dip can be envisaged as a photonic stop band for waveguide modes.[15,16] A more detailed description of the photonic band structure of our devices is given later. For higher pump energies, lasing occurs close to the Bragg wavelength (λ_{Bragg}) of the waveguides, and a narrow peak then dominates the emission. The PFO lasers operate at 455 nm and the F8DP lasers at 465 nm. The laser linewidth was measured in both cases to be about 0.8 nm, limited by the resolution of our spectrometer.

The dependence of the peak output intensity on the pump pulse energy is shown in Fig. 3. In both cases, a laser threshold is clearly observed: There is an abrupt change in the slope of the output versus input curves, followed by a linear increase of the output signal as the excitation energy is further increased. The threshold pump energy was $\sim$16.5 nJ for PFO and $\sim$4 nJ for F8DP. As reported elsewhere,[12,13] the spectral features of PFO and F8DP are similar, consistent with their common backbone structure. The emission of F8DP is, however, some 15 nm blueshifted with respect to PFO and has less weight in the higher order vibronic peaks. F8DP films show lower thresholds than PFO films of the same thickness,[12,13] consistent with a higher stimulated emission efficiency. The observation of a lower threshold in the F8DP laser is then in agreement with simple expectation. For pump pulse energies below these threshold values, the output emission corresponds to low intensity fluorescence from the polymers. When excited above threshold, the polymer lasers emit a bidirectional output beam normal to the waveguide plane.

We have also performed angle-dependent PL measurements to examine the effect of the grating microstructure on the polymer light emission and to investigate in more detail the lasing mechanism operative within our devices. For these measurements, the devices were excited at a very low intensity and the resulting light emission was analyzed as a function of wavelength and observation angle. Figure 4(a) shows a typical set of PL spectra obtained from a PFO-based laser structure, at observation angles (to the waveguide normal) $\varphi = 0°$, 2°, and 4°. The PL of a film spin coated on a flat spectrosil substrate is also shown for comparison. It is clearly seen that the presence of the grating microstructure in the substrate greatly modifies the spontaneous emission of the polymer. In particular, it produces a pair of strong narrow peaks that dominate the spectra. As the observation angle increases from normal incidence these peaks separate in wavelength. They correspond to PL that has been emitted into the TE_0 waveguide mode and subsequently Bragg scattered out of the waveguide by the fundamental component of

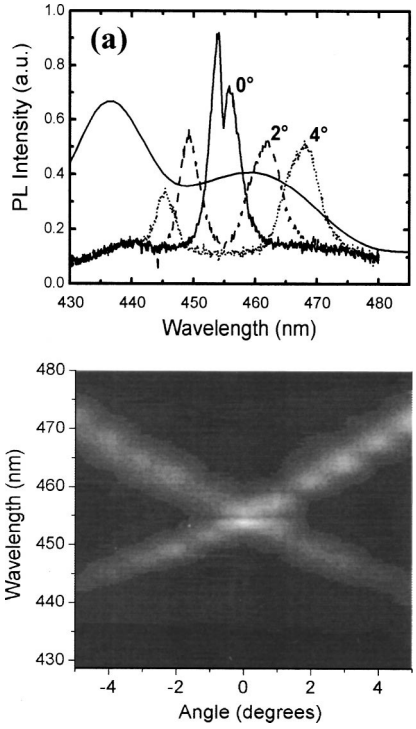

FIG. 4. (a) PL spectra from a PFO device at a range of observation angles (indicated). A typical spectrum from a PFO film on a flat substrate is also shown (solid line) and (b) Gray scale image of the angle-dependent PL. Brighter regions indicate stronger emission intensities.

the grating periodicity.[8] The dispersion of the TE_0 waveguide mode is more clearly seen in Fig. 4(b), which shows the results of the angle-dependent PL measurements in more detail. The changes in wavelength of the emission peaks with observation angle produce two discrete branches that anticross at normal incidence. The anticrossing region is situated at the Bragg resonance of the laser structure. In this spectral region, a reduction in the emission intensity is clearly observed: The periodic corrugations in the substrate induce a redistribution of the photonic density of states that produces a photonic stop band. In addition, we observe that the scattered intensity is consistently higher for the long wavelength branch than for the short wavelength branch. We attribute this asymmetry to either a difference in output coupling between the two band edges[8] or to an interplay between the gain and loss characteristics of the waveguides. In PFO slab waveguides, the peak optical gain occurs at $\lambda=466$ nm,[13] which favors and preferentially amplifies emission close to this wavelength. In contrast, the emission at the shorter wavelengths experiences lower gain and higher losses due to increased residual absorption and random scattering.

In the PFO-based devices, lasing occurs very close to λ_{Bragg} (inside the stop band) suggesting complex coupling characterized by gain modulation as the dominant mechanism for distributed feedback in these devices.[16] Gain modulation can be explained in terms of the periodically varying thickness of the polymer layer in the structures. Gain modulation has been reported in *m*-LPPP[6] and DOO–PPV[7] distributed feedback lasers. In contrast, in the F8DP-based devices, laser oscillation occurs at the long-wavelength band edge of the gap, suggesting a system dominated by index modulation (periodic variation of refractive index).[16] Index modulation has been reported in MEH–PPV[8] and in two-dimensional–DFB *m*-LPPP[9] lasers. Since the polymer deposition process was the same in both PFO and F8DP based devices, we attribute their different lasing behavior to the different thickness of the respective polymer layers. In particular, the smaller thickness of the polymer layer in the PFO lasers may have led to a more significant variation of its thickness across the devices, which consequently enhanced the contribution of gain modulation.

In summary, we have demonstrated lasing in PFO and F8DP devices in distributed feedback geometries. We used the third harmonic output of a small microchip laser as the pump source, thus demonstrating very compact, all solid-state polymer laser systems. The lasers operated in the blue (455 and 465 nm, respectively) and exhibited low threshold energies ($\geqslant$4 nJ). We showed that the presence of the grating greatly modified the emission characteristics of the polymers and induced a photonic stop band. The spectral location of laser oscillation in relation to the stop band was found to be different for the two lasers, suggesting the presence of different feedback mechanisms with a subtle interplay between gain and index modulation. This aspect of the operation of the devices will be the subject of further study.

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