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Semiconducting polymer distributed feedback lasers

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We have fabricated photopumped distributed feedback lasers by spin-casting thin films of the semiconducting polymer poly(2-butyl, 5-(2′-ethyl-hexyl)-1,4-phenylenevinylene) over gratings in silicon oxide. The lasers have two modes that each have a linewidth of 0.2 nm. The lasing wavelength was tuned from 540 to 583 nm by adjusting the period of the gratings. © *1998 American Institute of Physics.* [S0003-6951(98)01513-7]

Semiconducting (conjugated) polymers have properties that make them attractive as the gain material for solid-state lasers. They have high photoluminescence efficiencies and large cross sections for stimulated emission. Because of the Stokes shift between the emission and absorption wavelengths, they exhibit small self-absorption. As a result, semiconducting polymers exhibit gain at very low excitation densities at wavelengths that span the entire visible spectrum.[1] Through side-chain functionalization, conjugated polymers can be made soluble in common solvents, thereby enabling the fabrication of optical quality films by spin-casting from solution. Furthermore, since semiconducting polymers transport charge, they can be pumped electrically in a diode configuration.[2–4]

Amplified spontaneous emission (ASE) has now been observed at low pump intensities in a number of materials within this class when photopumping in a planar waveguide configuration.[1,5–9] Characterizing ASE is a useful way to demonstrate gain and to identify good laser materials; to actually make a laser, however, resonant feedback must be incorporated. A vertical microcavity can be formed by sandwiching a film between two dielectric or metallic mirrors.[10,11] This structure is relatively easy to pump electrically and has the desirable property that it emits a beam normal to the substrate. A disadvantage of vertical microcavities is that the distance traveled by light in the gain region during each pass through the cavity is short. Another simple way to make a high Q laser cavity is to form a microdisk by photolithography,[9] a microring by dip-coating a glass fiber,[12] or a microsphere by self-assembly of the polymer in the liquid state.[13] Although these structures are relatively easy to fabricate, they have the disadvantage that they emit light into a ring instead of a well defined beam. To obtain low threshold lasing with a well defined output beam, it is desirable to make an in-plane laser where photons travel a long distance ($>100\ \mu$m) during each pass through the gain region. In-plane Fabry–Pérot lasers can be made by reflection from the ends of the waveguide (due to the mismatch in refractive index of the organic and air.[14]) For conjugated polymers, however, the index of refraction is small compared to that of inorganic semiconductors. Moreover, it is difficult to form good facets with conjugated polymer films deposited from solution.

A convenient way to reflect light in a polymer waveguide is to incorporate a periodic modulation of the refractive index or the gain so that light is Bragg reflected.[8] Lasers of this type, known as distributed feedback (DFB) lasers, were first developed with films containing organic dyes[15] and have since been used extensively with inorganic laser materials.[16] The lasing wavelength of a DFB laser is close to the Bragg wavelength, $\lambda_{\mathrm{Bragg}}=2n_{\mathrm{eff}}\Lambda$ (n_{eff} is the effective refractive index of the waveguide and Λ is the period of the grating), and can be tuned by varying n_{eff} or Λ. DFB lasers made with a periodic modulation in the refractive index normally lase in two modes, one slightly below λ_{Bragg} and the other slightly above.[16,17] Single mode DFB lasers can be made by introducing a phase shift in the periodic modulation or by modulating the gain instead of the refractive index. In this letter, we report on photopumped DFB lasers made with the semiconducting polymer poly(2-butyl, 5-(2′-ethyl-hexyl)-1,4-phenylenevinylene) (BuEH-PPV) that have low thresholds and exhibit two narrow linewidth (0.2 nm) lasing modes at the wavelength predicted by the Bragg equation.

BuEH-PPV, a soluble alkyl-substituted PPV derivative, was chosen for these demonstration experiments because it has been shown to have high quantum efficiency photoluminescence (PL) (62% in neat films[18]) and a low threshold for gain narrowing.[1,19] DFB lasers were made by spin casting 150–350 nm thick films of BuEH-PPV from xylene solutions onto gratings in 1 μm thick SiO_2 layers that were grown by plasma enhanced chemical vapor deposition (PECVD) on silicon wafers [Fig. 1(a)]. The gratings had periods of 170–185 nm and were made by holographic lithography[20] and reactive ion etching with CHF_3. The grating depths, characterized with atomic force microscopy, ranged from 15 to 30 nm. A 1 μm thick layer of polymethylglutarimide (PMGI) was spin-cast over the BuEH-PPV to serve as a cladding layer which protects the waveguide from dust and scratches and prevents the BuEH-PPV from being exposed to air. PMGI has a refractive index of 1.54 at 550 nm and is transparent to visible light.

The refractive index of BuEH-PPV was measured by variable angle spectroscopic ellipsometry and found to be 1.76 in the plane of the film and 1.51 perpendicular to the

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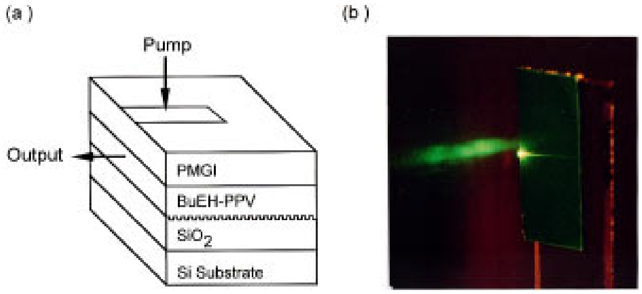

FIG. 1. (a) Schematic of the DFB laser structure and pumping configuration. The width of the pump stripe was 0.2 mm. The length of the pump stripe was typically between 0.5 and 2 mm. The thicknesses of the PMGI, BuEH-PPV, and SiO_2 layers were 1 μm, 0.15–0.35 μm, and 1 μm, respectively. Grating periods ranged from 170 to 185 nm. Grating depths ranged from 15 to 30 nm. (b) Photograph showing the edge emission onto a white screen placed 5 mm from the edge. Only 1 mm out of the 1 cm wide sample was photopumped. The irregularities in the beam are a result of the edge of the laser being rough.

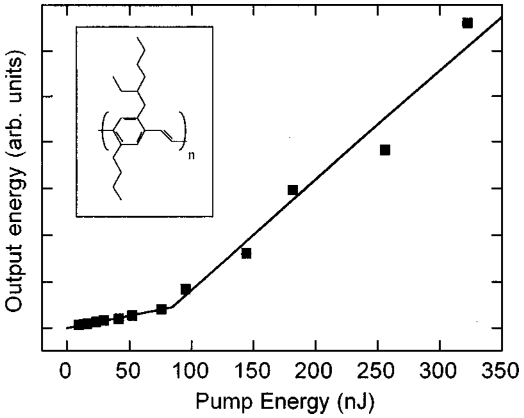

FIG. 2. Total output power (integrated over all wavelengths) from the edge as a function of pump energy. Inset: The BuEH-PPV repeat unit.

film at 550 nm.[21] The anisotropy is a consequence of the polymer chains lying preferentially in the plane of the substrate.[22,23]

As the thickness of the BuEH-PPV film is increased from 200 to 300 nm, the effective refractive index of the TE_0 mode of the waveguide increases from 1.62 to 1.67. Since n_{eff}, and in turn λ_{Bragg}, are sensitive to the BuEH-PPV film thickness, it is important that the films be uniform so that the resonant wavelength does not vary substantially over the region that is pumped. We found that for spin-cast films on DFB substrates, the lasing wavelength varied by less than 1 nm across the sample.

Samples were photopumped with 10 ns pulses of the first anti-Stokes line (435 nm) from a high pressure H_2 cell which was pumped by 532 nm light from a frequency doubled, 10 Hz, *Q*-switched Nd:YAG laser. The energy of the pulses was controlled with calibrated neutral density filters. An adjustable slit and a cylindrical lens were used to shape the beam into a 200 μm$\times$1 mm stripe. Samples were pumped at normal incidence with the long direction of the stripe perpendicular to the grooves in the substrate grating [Fig. 1(a)]. Because an edge bead forms during spin-casting, the substrates were cleaved (to remove the edge bead region) prior to measurement of laser properties. A strong beam of light was emitted from the edge of the sample [Fig. 1(b)]. Since the light was emitted from a region having dimensions of approximately 0.2$\times$200 μm, the output beam was highly divergent in the direction of the substrate normal due to diffraction. During measurements, most of the emitted beam was collected by a 10 cm focal length lens, dispersed with a 0.15 m focal length monochrometer using either a 300 or 2400 lines/mm grating and detected with a thermoelectrically cooled charge coupled device (CCD) camera.

The dependence of output energy emitted from the edge versus pump energy clearly exhibits a lasing threshold at 60 nJ/pulse (Fig. 2). Below threshold, the emission has the broad spectrum characteristic of spontaneous emission while above threshold the emission is dominated by a very narrow line from DFB lasing (Fig. 3). Since the narrow line is not present below threshold, it cannot be spontaneous emission filtered by the grating. Higher resolution spectra show that the narrow ''line'' is actually two lines, each of which has a linewidth of 0.2 nm (Fig. 3). If the laser were perfectly uniform and symmetric, the two lasing modes would be expected to have equal intensities. Slight imperfections can be sufficient to enable one mode to have a lower threshold than the other. When different spots on a sample were tested, we observed that the spacing between the modes did not vary substantially, but that the relative height of the two peaks with respect to each other did vary. In some cases there was only one lasing mode.

The observation of two narrow lines is strong evidence for DFB lasing and rules out ASE, which results in peaks with linewidths of 7 nm or more. Further evidence for DFB lasing was obtained by studying a collection of samples with different grating periods and samples without gratings. Above a threshold pump energy of 130 nJ/pulse, the samples without gratings all exhibited a narrow peak centered at 562 nm, which we attribute to ASE. The wavelength of the ASE emission is always centered at 562 nm because the luminescence spectrum of BuEH-PPV peaks near there; this is the wavelength where the net gain is highest.[19] By varying the length of the pump stripe, we observed that light was amplified by stimulated emission; the full width at half maximum (FWHM) of the emission spectrum was gain narrowed from

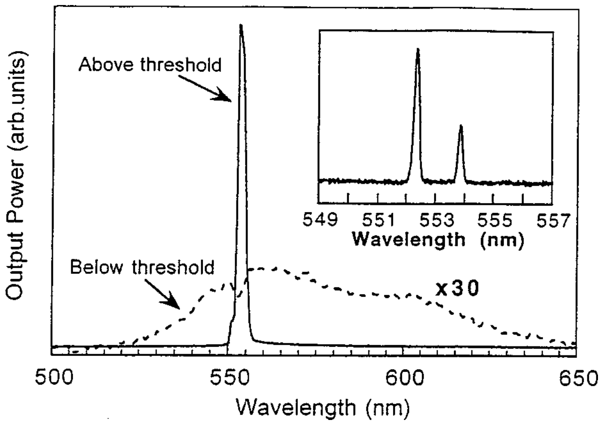

FIG. 3. Spectra taken below (dashed line) and above (solid line) lasing threshold. The below threshold spectrum was multiplied by a factor of 30. The grating period was 170$\pm$1 nm, the BuEH-PPV film thickness was 200$\pm$20 nm, the calculated n_{eff} was 1.62$\pm$0.02, and the calculated λ_{Bragg} was 551$\pm$6 nm. Inset: A high resolution spectrum taken above threshold showing two narrow laser emission lines (full width at half maximum of 0.2 nm).

70 to 7 nm as the length was increased. Narrower ASE linewidths could not be obtained because gain saturation limits the amount of amplification that can be achieved and stops the gain narrowing process. The full results of our study of ASE will be published elsewhere.[24]

In contrast, samples with gratings all lased at the wavelength predicted by the Bragg equation in two closely spaced modes with linewidths of only 0.1–0.3 nm (FWHM). By adjusting the grating period and BuEH-PPV film thickness, we were able to systematically vary the lasing wavelength from 540 to 583 nm, thus proving that the lasing results from the distributed feedback and demonstrating that conjugated polymer lasers can be tuned to lase over a wide range of wavelengths.

The polarization of the light emitted from the edge of the lasers was measured. Below the lasing threshold, the intensity of light polarized parallel to the substrate was three times the intensity perpendicular to it. Above threshold, the light was fully polarized parallel to the substrate, indicating that the lasing comes from a TE waveguide mode. We also measured the polarization of the ASE from samples without gratings. In this case one might expect that TE and TM modes would both be amplified and that the ASE light would not be polarized. We found, however, that even the ASE light was polarized parallel to the substrate with a polarization ratio of more than 100. This behavior arises because the polymer chains lie preferentially in the plane of the substrate. The first consequence of this anisotropy is that more light is emitted with a polarization parallel to the plane since conjugated polymers emit light that is polarized parallel to the chain axis. This explains the slight polarization of the below threshold emission. The second consequence is that BuEH-PPV has a higher refractive index for TE modes than for TM modes. Using the measured refractive indices, we modeled the waveguide mode shapes of the TE and TM modes. The TE_0 mode is well confined in the BuEH-PPV, but the higher order TE modes and all of the TM modes spread out beyond the BuEH-PPV and into the PMGI. Thus, the TE_0 mode experiences higher gain than the other modes; it is the mode that lases in a DFB structure and the mode that is most highly amplified in a waveguide structure that does not have feedback.

We have demonstrated that distributed feedback can be used to make low threshold lasers from thin films of a semiconducting polymer. Using distributed feedback we propose to make diode lasers in either of two ways: direct electrical pumping (inversion by electron and hole injection at opposite electrodes) or by placing the DFB structure monolithically onto a blue-emitting InGaN light-emitting diode (LED) which would be used to optically pump the DFB polymer laser. Currently, the thresholds of our lasers are approximately one order of magnitude too high for either of these approaches (the data in Fig. 2 indicate a threshold of ≈ 3 kW/cm^2; values as low as ≈ 1 kW/cm^2 were obtained in other samples). Since, the waveguide scattering losses in the films used in this study are relatively high, significant reduction in the threshold can be anticipated through straightforward improvements in film quality. Moreover, following Berggren *et al.*[8] and Koslov *et al.*,[14] the threshold for ASE and lasing can be significantly reduced by introducing a dilute amount of a laser dye such that energy transfer occurs between the host and the emitter. Experiments directed toward the achievement of diode lasers are underway in our laboratories and in many laboratories throughout the world.

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