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Intrinsic gain and gain degradation modulated by excitation pulse width in a semiconducting conjugated polymer

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ABSTRACT

We have previously reported that substantially higher optical gain values can be achieved in the conjugated polymer poly[2-methoxy-5-(2′-ethylhexyloxy)-p-phenylene vinylene] (MEH-PPV) through use of transient excitation conditions. In the present paper, we report on a systematic investigation of this behavior to elucidate the physical mechanisms involved, which enables us to distinguish between the fundamental intrinsic gain and an excitation induced degraded gain. Using pump laser pulses having temporal widths longer and shorter than the photoluminescence (PL) decay time of MEH-PPV, both quasi-steady-state (QSS) and transient excitation regimes are explored in our encapsulated waveguide heterostructures [Si(1 0 0)/SiO$_2$/MEH-PPV/poly(methyl methacrylate)]. Under transient excitation (25 ps pump pulses), *extremely large* optical gain is observed, reaching a value of 700 cm^{-1} at a maximum pump energy density of 85 μJ/cm^2. However, under QSS conditions (8 ns pulses), considerably lower gain coefficients are achieved with a maximum of ~130 cm^{-1} at an energy density of 2,000 μJ/cm^2; this factor of 5 decrease in optical gain performance is observed at the ***same excitation density*** as that for transient excitation using ps pulses. We have also employed unencapsulated waveguide structures [Si(1 0 0)/SiO$_2$/MEH-PPV/air], which allows us to achieve additional insight on gain degradation under QSS conditions. It is clear that the gain measured under transient conditions is more representative of the intrinsic gain whereas that determined in the QSS regime is degraded by defect-mediated dissociation of emissive states due to localized thermal and oxidative damage to the films. It is in the QSS regime in which most optical gain measurements to date have been performed. These results suggest that further optimization of MEH-PPV – and most likely other conjugated polymers – as a robust optical gain medium can be achieved by consideration of the excitation pulse width.

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1. Introduction

Conjugated polymers are actively being pursued as organic optical gain media for use in visible wavelength solid-state lasers. One of the most distinguishing features of conjugated polymers is their high luminescence quantum efficiency. In stark contrast to fluorescent organic molecules, which are typically used in dye-solvent lasers, conjugated polymers are capable of efficient light emission and light amplification in both solution and thin solid films. Furthermore, conjugated polymers can be directly integrated onto a silicon chip as active components at low cost as a consequence of their being solution processable. While all conjugated polymer-based lasers demonstrated thus far utilize an optical pumping source, the ultimate goal is to realize laser action under direct charge injection.

Despite recent progress in developing optically pumped conjugated polymer lasers, the fabrication of an electrically driven organic laser remains an extremely difficult task. One of the main obstacles is that conjugated polymers cannot yet achieve reasonable electrical current densities required to reach threshold [1]. That is, non-radiative losses associated with device architecture cause dramatic reductions in the net gain under electrical pumping. Such loss mechanisms include thermal and electrode related losses [1,2] as well as singlet-triplet annihilation [3] and strong polaron absorption [2,3], all of which become more problematic at higher bias. In the interim, however, alternative pumping schemes are being explored such as direct diode pumping of conjugated polymer lasers using, for example, integrated microchip lasers [4] or inorganic diode lasers [5]. To offset the cumulative

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losses resulting from charge induced absorption under electrical pumping and to enable the use of more compact and economical sources under optical pumping, conjugated polymers exhibiting low lasing thresholds and large net gains are highly desirable.

In previous reports, we have shown that the threshold and net gain behavior of MEH-PPV can be controlled by altering the morphology of the polymer films [6,7], and to a larger extent by optimizing the waveguide architecture [8]. Similar techniques have been used by other groups. For example, using planar waveguide structures formed by spin-casting thin films of MEH-PPV onto oxidized porous silicon substrates, Lahoz et al. [9] demonstrated that the amplified spontaneous emission (ASE) threshold could be controlled by changing the porosity, and hence refractive index, of the silicon substrate layer. Another effective approach for controlling the photophysical properties of conjugated polymers relies on host-guest chemistry, whereby excited states initially formed in an absorbing host are transferred non-radiatively to an emitting guest via long-range dipole-dipole interactions [10]. This cascade Forster transfer of energy shifts the emission spectrum to longer wavelengths, further from the absorption edge, leading to lower self-absorption losses and thus lower ASE thresholds.

While we have demonstrated extremely high optical gain in films prepared with different morphologies under transient pulsed excitation [6,7], our recent brief report [11] demonstrated the discovery of an excitation pulse width dependence of optical gain, which has enabled us to identify the intrinsic gain of MEH-PPV that has eluded others. In the current work, we report on our systematic investigation of a significant excitation pulse width dependence on optical gain and ASE threshold in photopumped films of MEH-PPV to understand the underlying gain degradation mechanisms and photophysics involved. Gain measurements are performed using the variable stripe length (VSL) technique on heterostructure waveguides formed from a thin layer of MEH-PPV sandwiched between an SiO_2 buffer and an index matched poly(methyl methacrylate) (PMMA) cover layer or air under different photoexcitation conditions. The data show that dramatically larger (5x) net gain is achievable under transient, as opposed to quasi-steady-state (QSS), excitation conditions. In addition, the onset energy for ASE is $30\times$ lower under 25 ps excitation compared to 8 ns excitation, although the effective excited state densities are essentially the same. On the basis of Fourier transform infrared (FTIR) spectral analysis on unencapsulated waveguides [Si(100)/SiO2/MEH-PPV/air], we conclude that the relatively long duration, high energy ns pump pulses introduce exciton-dissociating defects (carbonyl groups) into the polymer waveguide which effectively limits the achievable net gain. Our data also suggest that thermal degradation of the polymer can become relevant under QSS excitation. These findings offer an alternative approach for minimizing sample degradation and maximizing stimulated emission and gain that does not require special consideration of polymer morphology or device architecture.

2. Experimental procedures

MEH-PPV (Gilch type, M_n = 70,000–100,000 g/mol, $M_w/M_n \sim 5$) was purchased from Sigma-Aldrich and used as received. High concentration (10 mg/mL) solutions of MEH-PPV in distilled THF (Aldrich, anhydrous, ≥99.9%, inhibitor-free) were prepared by dissolving 50 mg of polymer in 5 mL of solvent under a high purity nitrogen environment. To facilitate the dissolution process, the polymer solutions were sonicated for 30 min in an ultrasonic bath. After stirring the solutions for 24 h in the dark at room temperature, they were sonicated for an additional 90 min immediately prior to film formation. Using a Laurell Technologies WS-400 spin coater, optical quality waveguides were fabricated by spin casting

130–135-nm-thick films from the MEH-PPV/THF solutions at 2000 rpm onto cleaned SiO_2(1-μm-thick)/Si(100) substrates. The samples were then heated at 60 °C under vacuum for 30 min to eliminate any residual solvent and allowed to cool overnight to room temperature. Encapsulated planar waveguides were formed by spin-casting a 450–500-nm-thick cover layer of poly(methyl methacrylate) (PMMA) from 50 mg/mL PMMA/ THF solution directly on top of the MEH-PPV films. Addition of a PMMA cover layer provides some protection of the MEH-PPV films from excessive oxidative degradation under optical excitation and increases optical confinement of the guided mode [8]. Shi et al. [12] pointed out that for multilayer spin-cast films, the interfacial regions are susceptible to enhanced degrees of interchain interactions due to re-dissolution of the polymer chains at the surface of the previously cast film. To minimize these effects, the PMMA cover layer was cast from THF solution, which is well known to hinder aggregate formation [13–15] and evaporates rapidly at high spin speeds. This should inhibit MEH-PPV/solvent interactions. MEH-PPV and PMMA film thicknesses were chosen such that mono-mode waveguides were formed. To avoid nonuniformity in film thickness near the edge of the samples, the substrates were cleaved before optical measurements.

The in-plane (ordinary) refractive index of the MEH-PPV films at 640 nm, as determined by spectroscopic ellipsometry, is 1.84, which agrees with previous reports [9]. Photoluminescence (PL) and variable stripe length (VSL) measurements were performed using two different laser systems. Except for the pump lasers, all other aspects of the measurement systems were the same. The samples were initially pumped with vertically polarized 25 ps pulses delivered at a repetition rate of 10 Hz using a frequency doubled (λ = 532 nm) regeneratively amplified mode-locked neodymium-doped yttrium aluminum garnet (Nd:YAG) laser (EKSPLA PL2143). Because the duration of the 25 ps pump pulses are short relative to the PL decay time of MEH-PPV, which has been reported to be $\sim$300 ps [16,17], this experiment was performed under non- steady-state or transient conditions. In subsequent measurements, the samples were pumped with vertically polarized 8 ns pulses delivered at a repetition rate of 10 Hz using a frequency doubled (λ = 532 nm) Q-switched Nd:YAG laser (Continuum MiniLite II). In this case, the experiment was performed under quasi-steady-state (QSS) conditions since the excitation pulse duration was longer than the PL decay time of MEH-PPV. Two spherical plano-convex lenses with focal lengths of 80 and 200 mm collected and collimated the emission from the edge of the films and focused it onto the entrance slit of a monochromator coupled to a liquid nitrogen cooled charge-coupled device (CCD) operating at −100 °C. The collection lens was positioned at a distance of 80 mm (the focal length of the lens) from the sample edge. The energy of the pulses was controlled using a set of calibrated neutral density filters. A cylindrical lens (focal length f = 100 mm) was used to shape the pump beam into a stripe. The center portion of this stripe was then spatially filtered through a stationary metal slit to create a thin, 100 μm × 1 mm, excitation stripe on the sample surface. One end of the excitation stripe was positioned at the cleaved edge of the sample. The stripe length was varied by superimposing an adjustable shield directly over the fixed metal slit, which was placed in close proximity to the sample surface ($\sim$100 μm) to minimize diffraction effects. We have verified that the collection efficiency and excitation intensity profile were effectively constant across the lengths of stripe used. All of the experiments reported here were performed under ambient conditions and emission spectra were integrated over 1–70 pump pulses.

The vibrational bands of MEH-PPV films deposited on SiO_2(1-μm-thick)/Si(100) substrates were measured using a Varian-640 Fourier transform infrared (FTIR) spectrometer in attenuated total reflectance (ATR) mode (Pike Miracle ATR). Absorption spectra