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Enhancement of optical gain and amplified spontaneous emission due to waveguide geometry in the conjugated polymer poly[2-methoxy-5-(2’-ethylhexyloxy)-p-phenylene vinylene]

Zach E. Lampert, John M. Papanikolas, and C. Lewis Reynolds, Jr.

Department of Materials Science and Engineering, North Carolina State University, Raleigh, North Carolina 27695-7919, USA

Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina 27599, USA

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We report enhanced amplified spontaneous emission (ASE) and optical gain performance in a conjugated polymer (CP)-based thin film waveguide (WG) Si(100)/SiO2/poly[2-methoxy-5-(2’-ethylhexyloxy)-p-phenylene vinylene] (MEH-PPV) by encapsulating the active layer with a transparent dielectric film of poly(methyl methacrylate) (PMMA). With index matched SiO2 and PMMA claddings, symmetric WGs are formed that exhibit increased mode confinement and reduced propagation loss enabling lower ASE threshold (40%) and higher optical gain (50%) compared to Si(100)/SiO2/MEH-PPV/air asymmetric WGs. An extremely large net gain coefficient of 500 cm\(^{-1}\) is achieved under picosecond pulse excitation, which is >4 times larger than values previously reported in the literature. Fabrication of symmetric WGs requires no complex processing techniques, thus offering a simple, low-cost approach for effectively controlling the ASE behavior of CP-based WGs and related optical devices.

Conjugated polymers (CPs) are materials that exhibit the optical and electrical properties of semiconductors while still retaining the durability and processability of plastics. Conjugated polymers are also intrinsically four-level systems with large gain cross-sections making them ideal candidates for cost-effective optical components integrated on silicon. Although optically pumped Si-polymer hybrid structures have exhibited lasing action, achievement of stimulated emission under electrical pumping remains unsuccessful, largely because CP films cannot yet accommodate the current densities required to potentially reach threshold. Moreover, non-radiative absorption losses associated with device architecture severely degrade optical gain. While a direct injection polymer laser remains the ultimate scientific goal, alternative approaches are being explored such as indirect electrical pumping using, for example, light emitting diodes (LEDs) or pulsed microchip lasers as electrically driven optical pump sources for CP-based laser devices. Further optimization is required, however, and CPs exhibiting lower thresholds and higher gain are highly desirable.

We have previously shown that threshold and gain characteristics of poly[2-methoxy-5-(2’-ethylhexyloxy)-p-phenylene vinylene] (MEH-PPV) can be controlled by varying the packing morphology of the polymer chains and to a larger extent by optimizing the duration of the excitation pump pulses. Other approaches focus on the fabrication and design of improved device architectures. For example, Martini et al. have shown that encapsulation of MEH-PPV polymer chains in the nanopores of a silica host dramatically improves amplified spontaneous emission (ASE) threshold behavior in MEH-PPV waveguide (WG) structures. These improvements were attributed to the nanoscale positioning and spatial alignment of the polymer chains. Threshold reductions have also been achieved by increasing confinement of the guided mode in MEH-PPV WGs formed on high-porosity porous silicon substrates. Although these device architectures facilitate low threshold ASE, their fabrication is time-consuming and requires complex processing techniques. Thus, one concludes that alternative approaches must be explored if CPs are to be adopted as low-cost optical components integrated on silicon.

Here, we demonstrate significant enhancement of ASE performance in an active planar WG based on the conjugated polymer MEH-PPV. By spin-coating thin dielectric films of poly(methyl methacrylate) (PMMA) on top of Si(100)/SiO2/MEH-PPV WGs, symmetric waveguide (SWG) heterostructures are formed that exhibit lower ASE threshold and higher net gain compared to unencapsulated Si(100)/SiO2/MEH-PPV/air asymmetric WGs. Symmetric WG fabrication is low-cost and does not require complex processing or specialized equipment, thus offering an alternate route for effectively controlling the ASE characteristics of CP-based active WGs and edge-emitting distributed feedback laser devices. Note that while ASE threshold reductions have recently been demonstrated using glass/indium-tin oxide (ITO)/SiO2/MEH-PPV/Ag SWG structures, the performance enhancements were achieved based on optimization of the SiO2 spacer layer thickness; however, there was no analysis provided regarding the influence of WG symmetry and mode confinement on threshold and gain.

MEH-PPV was purchased from Sigma-Aldrich and used as received. Asymmetric WGs of Si(100)/SiO2/MEH-PPV/air were fabricated by spin coating films of MEH-PPV from 1.0% w/v chlorobenzene solution onto Si(100) substrates with a 1-μm-thick layer of thermally grown oxide.

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samples were then heated to 80 °C under vacuum for 60 min to remove residual solvent. Symmetric WG structures of Si(100)/SiO_x/MEH-PPV/PMMA were prepared by spin coating a layer of PMMA directly on top of the MEH-PPV films from a 5.0% w/v solution of tetrahydrofuran (THF). It has been shown that the interfacial regions between successive layers of multilayer spin-cast films are prone to enhanced degrees of interchain interactions, which is a consequence of re-dissolution of polymer chains at the surface of the previously cast film.25 To minimize these effects, the PMMA cladding layer was cast from solutions containing THF as the solvent, which is well known for its ability to hinder aggregate formation.1,26–28 Also, the THF solvent evaporates nearly instantaneously at a spin speed of 2000 rpm, which effectively limits MEH-PPV/solvent interactions. The thicknesses of the MEH-PPV (PMMA) films, as measured by atomic force microscopy, were 120–125 nm (450–500 nm). The Si substrates were cleaved before the optical measurements to avoid nonuniformity in film thickness near the edge of the samples.

The WGs were transversely pumped using a frequency doubled (λ = 532 nm) regeneratively amplified neodymium-doped yttrium aluminum garnet (Nd:YAG) laser operating at 10 Hz. The laser pulses were 25 ps in duration and vertically polarized. The energy of the pulses was controlled using calibrated neutral density filters. Since the photoluminescence (PL) lifetime of MEH-PPV (≈300 ps)29,30 is longer than the duration of the excitation pump pulses (25 ps), the measurement conditions are non-steady state. The pump beam was focused with a cylindrical lens to create a narrow excitation stripe, 100 µm wide and of variable length on the sample surface. We have verified that the collection efficiency and intensity profile were effectively constant across the lengths of stripe used. Emission was detected from the edge of the WGs using a spectrometer attached to a charge coupled device. In the subsequent discussion, the asymmetric and symmetric waveguides will be referred to as AWGs and SWGs, respectively. These samples constitute planar WGs since the refractive index of MEH-PPV (n = 1.84) is larger than SiO_x (n = 1.46) buffer and air (n = 1) or PMMA (n = 1.48) cover layers. All of the experiments were performed under ambient conditions.

Figure 1 shows the evolution of the PL spectra for AWGs and SWGs upon increasing the pump energy density. At low pump fluence (<5 µJ/cm^2), the spectra are broad and exhibit an electronic transition at 590 nm followed by vibronic progressions at 637 and 695 nm, which is characteristic of spontaneous emission. With increasing pump energy, spectral narrowing occurs at the peak of the emission spectrum dominated by the 0-1 vibronic signature at ~637 nm due to ASE. At sufficiently high pump energy density the broad PL spectrum collapses into a single narrowed peak with a full width at half maximum (FWHM) of ~10 nm (see Fig. 2 inset).

Accompanying spectral narrowing, the WGs exhibit a dramatic increase in PL efficiency above a threshold value of the pump energy density E_th, resulting in a sharp increase in slope as observed in Fig. 2. We define E_th as the pump energy density at which the PL intensity (FWHM) of the 0-1 transition is reduced to half its initial value at low pump energy. From the FWHM vs. pump energy density plot (Fig. 2 inset), the threshold values for AWGs and SWGs are 12 µJ/cm^2 and 7.5 µJ/cm^2, respectively, which means that SWGs require ~40% less pumping fluence to achieve threshold.

As discussed below, two contributing factors are responsible for the reduction of ASE threshold in SWGs, namely enhanced spatial confinement of the guided mode and reduced WG propagation loss.

The fundamental WG modes and associated field profiles were determined using a one-dimensional mode solver.31 Figure 3 shows the experimental geometry of the AWGs and SWGs with the relevant simulation parameters that were used in the WG calculations. The refractive index profile and electric field intensity distribution of the fundamental transverse electric (TE0) guided mode for AWGs and SWGs at λ_ASE are shown in Fig. 4. Since transverse magnetic (TM) and higher order TE modes are not supported, only the fundamental TE0 mode was considered in this study.

As shown in Fig. 4(a), the spatial distribution of the guided mode in the AWG exhibits an asymmetric intensity profile with a significant fraction of the mode penetrating into the SiO_x layer. Relative to the AWG, an increase in WG

![FIG. 1. Normalized edge emitted PL spectra collected from AWGs (a) and SWGs (b) at different pump energy densities using a pump stripe length of 0.1 cm. Inset: chemical structure of MEH-PPV.](image-url)

![FIG. 2. Dependence of integrated emission intensity on pump energy density for AWGs (triangles) and SWGs (squares). Inset: PL linewidth (FWHM) vs. pump energy density. The pump stripe length is 0.1 cm.](image-url)

![FIG. 3. Schematic of asymmetric (a) and symmetric (b) WG structures showing refractive index and layer thickness values.](image-url)
The confinement factor is a measure of the extent to which the guided mode in a one-dimensional planar WG structure is confined to the active layer. With a larger fraction of light confined to the active layer, the threshold pump fluence, and $g_{\text{max}}$ is the maximum net gain coefficient.

The confinement factor $\Gamma$ of a guided mode in a one-dimensional planar WG structure is given by:

$$\Gamma \approx \frac{\int_{d/2}^{d/2-a} Sdx}{\int_{-\infty}^{\infty} Sdx},$$

where $d$ is the MEH-PPV film thickness, $\Lambda$ is the effective absorption length ($\Lambda = \frac{1}{\alpha_{abs}} = 61$ nm, where $\alpha_{abs}$ is the absorption coefficient at the pump wavelength), and $S$ is the Poynting vector which describes the density of power flowing through the WGs.

The confinement factor is the ratio of the guided mode's intensity distribution to the total intensity distribution. Using the WG loss and confinement factors in Table I, we can estimate relative changes of the pump flux $\phi_{th}$ at the ASE threshold for an intrinsic four-level system like MEH-PPV using the following expression for $\phi_{th}$ under steady-state excitation:

$$\phi_{th} \approx \frac{2\Delta}{1+\alpha L \sigma_{em}},$$

where $\tau$ is the excited state lifetime, $\sigma_{em}$ is the stimulated emission cross-section, and $L$ is the pumped length. The gain performance of the WGs was measured using the variable stripe length (VSL) technique, which involved exciting the films with a narrow pump stripe of variable length. The edge emitted peak intensity $I_{\text{th}}$ at $\lambda_{\text{ASE}}$ for SWGs and AWGs was measured as a function of the stripe length and the resulting curves fit the expression

$$I(\lambda) = \frac{AP_o}{g(\lambda)} \left( e^{g(\lambda)L} - 1 \right),$$

where $g(\lambda)$ is the net gain coefficient, $L$ is the pump stripe length, and $AP_o$ describes spontaneous emission.
shows the peak intensity at $\lambda_{ASE}$ for AWGs and SWGs as a function of the excitation stripe length at various pump energy densities.

Fitting of the data in Fig. 6 to Eq. (3) is given by the broken lines in the figure. Only the exponential portion of the experimental data prior to the onset of gain saturation was included in the fits. At a pump energy density of $5 \mu J/cm^2$, no amplification is present and the peak intensity grows sublinearly with increasing stripe length. However, an exponential increase in ASE peak intensity is clearly observed for the WGs at a pump energy density of $30 \mu J/cm^2$. This exponential increase is accompanied by spectral narrowing (Fig. 6 Insets) and occurs above a threshold excitation length $L_t$, which decreases with increasing pump energy indicating higher gain. It should be noted that no photodamage to our samples was observed under our picosecond pulsed excitation conditions.

Shown in Fig. 7 are the net gain coefficients as a function of the pump energy density. Each value represents the average of at least three separate measurements. At a low pump energy density of $5 \mu J/cm^2$, the net gain coefficient for the AWGs and SWGs are $-10$ and $-8 \text{ cm}^{-1}$, respectively, indicating a loss. These loss values are in good agreement with the loss values obtained using the SES technique (Table I), which confirms that our experimental setup for VSL measurements is configured properly.

With increasing pump energy density, both the AWGs and SWGs exhibited positive net gain that scaled approximately linearly with the pump energy until eventually saturating. Extremely large gain coefficients of 330 and 500 cm$^{-1}$ were achieved for AWGs and SWGs, respectively, at a maximum pump energy density of 85 $\mu J/cm^2$. Thus, in addition to reducing the ASE threshold, the increase in WG symmetry also serves to significantly enhance optical gain. Again, we attribute this improvement to the increased overlap between the optical WG mode and CP gain layer in the SWG relative to the asymmetric one. This is also consistent with what one would expect based on the expression for the net gain of a four-level system given by $g_{net} = g_{mod} - \alpha \approx \Gamma \sigma_{em} N_{ex} - \alpha$, where $\alpha$ is the loss, $\Gamma$ is the confinement factor, $\sigma_{em}$ is the stimulated emission cross section, $g_{mod}$ is the modal gain, and $N_{ex}$ is the excitation density. Total WG loss is typically much smaller than the modal gain and can therefore be neglected. Larger net gain is therefore expected from MEH-PPV WGs exhibiting larger optical confinement. Using the calculated confinement factor values (Table I), the four-level gain equation (above) predicts a factor of 1.3 increase in the maximum net gain for SWGs relative to AWGs, which is in reasonable agreement with the experimentally observed factor of 1.5. In addition to the significant enhancement of optical gain and lowered threshold for ASE that we have reported here, Richardson et al. have shown that encapsulating the MEH-PPV WG layer improves operational lifetime and stability by minimizing photooxidation. While these authors acknowledged the dependence of the waveguiding properties on the index profile of the device, the quantitative effect on optical gain was not investigated.

In summary, we have demonstrated a simple, low-cost approach for enhancement of ASE performance in MEH-PPV films using symmetric WGs with optimized distribution of the TE$_0$ guided mode in the CP gain layer. A low threshold of 7.5 $\mu J/cm^2$ and extremely large net gain coefficient of 500 cm$^{-1}$ were achieved in symmetric WGs under ps pulse excitation, compared to 12 $\mu J/cm^2$ and 330 cm$^{-1}$ for asymmetric WGs. These gain coefficients are a factor of 4 or higher than those previously reported in the literature. The efficacy of our methodology is attributed to enhanced optical confinement and reduced propagation loss of gain guided light in the symmetric WG structures. Fabrication of symmetric WGs requires no complex processing techniques, thus offering simpler access to improved ASE characteristics in CP-based WGs and related optical devices.

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31Software: MODE Solutions, version 5.0, Lumerical Solutions, Inc.
38Number of reflections proportional to tan θ/2, where θ is the propagation angle of the guided mode.