Diode pumped distributed Bragg reflector lasers based on a dye-to-polymer energy transfer blend

A. E. Vasdekis, G. Tsiminis, J.-C. Ribierre, Liam O’ Faolain, T. F. Krauss,
G. A. Turnbull and I. D. W. Samuel

Organic Semiconductor Centre & Ultrafast Photonics Collaboration, SUPA, School of Physics and Astronomy, University of St Andrews, St Andrews, Fife, KY16 9SS, UK

Abstract: We report the demonstration of a compact, all-solid-state polymer laser system comprising of a Gallium Nitride (GaN) semiconductor diode laser as the pump source. The polymer laser was configured as a surface emitting, distributed Bragg reflector laser (DBR), based on a novel energy transfer blend of Coumarin 102 and the conjugated polymer poly(2-methoxy-5-(2’-ethylhexyloxy)-1,4-phenylene vinylene). In this configuration, diode pumping was possible both due to the improved quality of the resonators and the improved harvesting of the diode laser light.

©2006 Optical Society of America

OCIS codes: (250.3680) Light-emitting polymers; (140.3380) Laser Materials; (140.5960) Semiconductor lasers; (250.7270) Vertical emitting lasers; (230.3990) Microstructure devices;

References and links

1. Introduction

In recent years, semiconducting (conjugated) polymers have emerged as an attractive new gain medium for widely tuneable visible lasers [1-6]. Several families of materials have been studied, though much of the work has concentrated on derivatives of poly(paraphenylene-vinylene) and poly(fluorene) [4-6]. These are highly fluorescent and exhibit little concentration quenching, allowing them to be used in the undiluted solid state. In such a configuration, they are electroluminescent, suggesting the possibility of electrically excited plastic lasers. The polymers can also be readily processed from solution to form low-loss optical waveguides and compact diffractive resonators. Such lasers offer new possibilities for spectroscopic applications, including ultrasensitive chemical sensing [7]. While direct electrical pumping remains a major outstanding challenge optically pumped polymer lasers have developed to become very attractive visible sources [1-6]. Lasing thresholds of polymer distributed feedback (DFB) lasers are now commonly low enough to be pumped by pulsed microchip lasers [8]. GaN diode-laser-pumped organic lasers based on polyfluorene derivatives have recently been reported [9, 10].

In this paper we demonstrate diode-pumped organic lasers based on the poly(paraphenylene-vinylene) derivative MEH-PPV. To achieve the very low oscillation thresholds required for direct diode pumping, we combine a novel surface-emitting resonator structure with an energy-transfer gain medium. The gain medium is to the best of our knowledge, the first example of a concentrated laser dye host doped with a luminescent polymer for lasing applications. We show that efficient energy transfer is possible from the dye to the polymer and describe the photo-physical performance of the gain medium for diode laser excitation. We then describe the operation principle of the DBR polymer cavities and finally the operating characteristics of the resulting devices.

2. Dye-to-polymer energy transfer

MEH-PPV is a well-known prototypical polymer, readily available from a variety of commercial sources. However, its strongest absorption is at 500 nm (Fig. 1) hindering thus the efficient harvesting of the GaN diode violet emission. To overcome this, our strategy was to employ non-radiative energy transfer by blending the emissive species in an appropriate host [9, 11-14]. A potential host would be another conjugated polymer, but polymer blends tend to phase separate, particularly when mixed in similar quantities.

We explore instead the blending of the MEH-PPV with the dye molecule Coumarin 102. The dye fluoresces at the absorption maximum of the MEH-PPV and also exhibits a strong absorption band at the GaN laser emission wavelength. We study the energy transfer process from a concentrated dye film [14] and its viability for lasing in the polymer guest. The study involved the measurement of the absorption and photoluminescence spectra, the absolute photoluminescence quantum yield (PLQY) and the amplified spontaneous emission thresholds of thin films.
The MEH-PPV (American Dye Source Inc.) and the Coumarin 102 (Lambda Physik) were first co-dissolved in chlorobenzene in a range of blend ratios, and spin-cast onto fused silica substrates to form films ~100 nm thick. We find that we can form good quality films for a wide range of blend ratios, even at near equal weights. Figure 1(a) shows the absorption of solid-state blends of various weight fractions of Coumarin 102, plus the absorption of the dye in chlorobenzene solution and the emission wavelength of the GaN laser (black arrow). We find we can significantly increase the absorption at the diode laser wavelength relative to that of the MEH-PPV. In addition, for all these blends the emission is dominated by the MEH-PPV photoluminescence spectrum. This result is characteristic of efficient energy transfer, but does not by itself confirm its presence, as the concentrated dye film is also likely to exhibit a rapid non-radiative decay path that will quench its emission, competing with the energy transfer.

The PLQY is the ratio of photons emitted to photons absorbed, and is measured for films mounted inside an integrating sphere in order to collect light emitted in all directions [15]. In Fig. 1(b), the PLQY is plotted as a function of the doping concentration for both the direct excitation of the polymer at 514 nm, and excitation into the dye absorption band at 407 nm. A substantial increase in the blend PLQY is achieved as compared to neat MEH-PPV films for increasing dye concentration. This increase is indicative that non-radiative decay in the polymer is lowered due to reduced intra-molecular interactions and self absorption in the blends. The similarity in PLQY values between direct (514 nm) and indirect (407 nm) excitation of the MEH-PPV confirms that we do have an efficient energy transfer (> 80% for the 50:50 wt. % blend) from the dye to the polymer.

The ASE experiments were performed by exciting the films with the 407 nm emission from an OPO (Continuum Panther EX) focused to a stripe with dimensions 170 μm by 3.8 mm. The spectrum of the blend emission was detected from the edge of the film using a CCD spectrograph for a range of excitation densities. For excitation above a critical pumping density, we observe the onset of ASE in each of the films, characterized by a gain narrowing of the edge-emitted spectrum. The ASE was centered at 632 nm for the blends and at 621 nm for the neat MEH-PPV, with linewidths of ~ 9 nm, confirming thus the efficient energy transfer from the dye molecule to the MEH-PPV. The 11 nm difference follows the red-shift in the MEH-PPV absorption in the blends. From Fig. 1(b) (blue line) it can be observed that in terms of incident pump energies a clear threshold minimum occurs at the concentration of 50:50 wt.%. When correcting for the amount of light absorbed in each blend, the ASE thresholds become comparable indicating the successful light harvesting of the blend, while maintaining the amplifying properties of the conjugated polymer. At high concentrations...
 (>50% per weight), the ASE threshold increases and a possible explanation for this effect may be the increased scattering losses due to the formation of aggregates. In the following experiments we used the optimal blending concentration of 50:50 wt. %.

3. Distributed Bragg reflector polymer lasers

DFB polymer lasers have been widely studied in the past and have been shown to exhibit enhanced performance in terms of low thresholds and collimated emission [8]. A thin polymer film is spun on top of a grating and a standing wave is created due to interference effects originating from the periodic modulation of the refractive index. This modulation however can act as a source of loss due to mainly two possible mechanisms. The first one is the diffractive output coupling that provides the advantageous surface emission in 2nd order DFB lasers, but has been identified as a major source of loss in these devices [16]. A further probable source of loss is the incoherent scattering associated with the inevitable surface non-uniformity of a polymer film spun on a corrugated substrate. In both cases lower net-gain is expected.

In order to further improve the performance of polymer solid-state lasers, we investigate DBR resonators. In DBR lasers, the amplifying medium is placed between two Bragg mirrors that provide the necessary feedback for lasing. By this means, the areas of population inversion are separated from the Bragg gratings and hence both of the aforementioned possible losses are addressed. In Fig. 2 a general schematic of such a structure is shown: the planar polymer film acts as an amplifier and the adjacent gratings form the resonator. The optical excitation is centered in the planar polymer film and the emitted photons can form a standing wave due to the reflection from the gratings. If a 2nd order grating is used, the amplified light will be both reflected in the plane of the guide and scattered from the surface, thus forming a compact, surface-emitting laser.

Such polymer lasers have been previously investigated, where the mirror separation was of the order of 1 mm [17, 18]. In addition, a lot of attention has been focused on similar structures, namely the organic VCSEL type of lasers (or microcavities) that nonetheless entail certain drawbacks, such as the additional step of the mirrors’ evaporation but also the short gain length limited by the thickness of the organic film [11, 19]. In contrast to these reports, the mirror separation in our experiments was kept within the range of 10 to 110 μm in order to achieve increased gain length but also to avoid severe multi-mode operation and the associated gain competition. In addition, for these cavity lengths we could achieve high excitation densities even for the low pulse energies that are currently available from GaN diode lasers.

In the current experiments, the resonators were defined on a 140 nm film of poly(methyl methacrylate) (PMMA) using electron-beam lithography (Hybrid LEO Gemini 1530 SEM/RAITH ELPHY lithography system) at 30 kV. In order to improve the resolution of the lithography, a 15 nm gold and a 20 nm PEDOT film were added on top of the resist. The
pattern was subsequently transferred onto a fused silica substrate using reactive ion plasma chemistry. In each resonator, both mirror gratings had a period of 410 nm, thus providing in-plane reflectivity and surface emission of the laser light via second and first order diffraction respectively. The length of each mirror was 41 μm (100 layers) providing high reflectivity for the laser field [20]. In addition, the substrate area between the mirrors was etched to form a channel waveguide and hence confine the light in the lateral direction to the feedback. A typical grating structure for a mirror separation of 10 μm is shown in the SEM image of Fig. 2. Additionally, the mirror separation was varied in order to confirm the principle of operation by studying the resonant behaviour for a range of lengths and also to identify the optimal length.

4. Diode pumping

The pump source was a GaN diode laser (Jobin Yvon Horiba) with maximum pulse energy of 0.67 nJ, pulse duration of 1 nsec and a repetition rate of 10 kHz. The astigmatic and highly divergent output beam was focused using a spherical lens to an elliptical spot size with a diameter along the major and minor axis of 76 μm and 66 μm respectively. In the optical experiments care was taken so that the major axis of the excitation area was parallel to the resonant direction of the cavity and the polarisation of the pump light parallel to the grating grooves. The excitation wavelength was 409 nm, matching the absorption of the host molecule. The emission was collected normal to the surface of the polymer film using a fibre coupled CCD spectrometer.

In Fig. 3(a) a typical emission spectrum below and above threshold is shown for a mirror separation of 20 μm. Below threshold, the spontaneous emission couples to four distinct optical modes at 624 nm, 625.7 nm, 628.2 nm and 630.4 nm. Angular dispersion measurements indicated that the modes at the shortest and longest wavelength correspond to the Bragg scattered modes that originate from the periodic nature of the gratings [21]. These modes appear at the edges of the stop-band at normal incidence and shift in wavelength for different scattering angles. The presence of these modes is enhanced by the optical excitation of the grating mirrors since the excitation spot in our experiments is larger than the mirror separation.

The intermediate modes at wavelengths 625.7 nm and 628.2 nm are the resonant modes of the DBR cavity. These modes appear within the stop-band and are excited only when the pump light is centered between the Bragg mirrors. These modes do not exhibit such strong angular dispersion and from their free spectral range we deduced a total cavity length of 49 μm corresponding to the actual mirror separation length plus a photon penetration length of ~14.5 μm at each mirror. In addition, respectable Q-factors (Δλ/λ ~10^3) were obtained confirming the high quality of the cavity.

Fig. 3. (a). The emission spectra above (0.67 nJ) and below threshold (0.27 nJ), where both the DBR and ‘mirror modes’ are shown. (b) The input-output relationship for the laser peak at 625.6 nm (blue) and the spontaneous emission at 632.1 nm (red). The lines are a guide to the eye. (c) The normalized emission spectra for different excitation densities. The normalization level was chosen at the wavelength of 632.1 nm corresponding to the spontaneous emission and is denoted by the blue arrow.
Above a pump energy of 0.42 nJ, we observe a change in the emitted light. This can be seen in Fig. 3(b). There is an increase in growth of the DBR mode at 625.6 nm and a flattening of the spontaneous emission at 632.1 nm. The faster growth of one of the modes and the pinning of the others is a clear indication of lasing [1]. This behaviour can also be seen in Fig. 3(c), where the emission spectra are normalized at the wavelength of 632.2 nm. Below threshold, the spectra evolve linearly with the pump intensity and hence completely overlap when normalized. Above threshold, the laser peak increases faster than the background indicating the non-linearity associated with stimulated emission. The same behaviour was observed for 30 and 50 μm cavity lengths, but with more longitudinal modes within the stopband, and a decreasing free spectral range, for increasing cavity length. Finally, when using a frequency doubled Q-switched Nd:YVO₄ microchip pump laser that allowed for higher excitation densities, the same behaviour was observed with the lasing mode rapidly growing to completely dominate the surface emission. In addition, with this pump laser we also found that the DFB lasers have higher thresholds than the DBR.

5. Conclusion

In conclusion, we have demonstrated a solid-state polymer laser pumped with an inorganic diode laser. We used a novel blend based on the dye Coumarin 102 and the conjugated polymer MEH-PPV, both of which were commercially sourced. This allowed the efficient transfer of the GaN pump excitation to the conjugated polymer. In regards to the cavity optimization, we used a polymer DBR resonator that acted as a low threshold, surface-emitting laser. In comparison to 2nd order DFB lasers, we attribute the optimised performance to the separation of the Bragg gratings with the amplifier. The latter allowed the reduction of coherent and incoherent scattering losses and cavity modes of high quality factors.

Acknowledgments

We are grateful to EPSRC for financial support.