Design and Characterisation of Blue Polymer Lasers

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Submitted in fulfillment of the requirements of the degree of

Doctor of Philosophy
Für mini Frau Pascale und min Vater Domenico
für iri Liebi und Unterstützig

To my wife Pascale and my father Domenico
for their love and support
Declaration

This thesis describes the work done in the Experimental Solid State Physics group of Imperial College London, under the supervision of Professor Donal D.C. Bradley. Except where specific reference is made to the work of others, the results presented herein are the product of my own work.
Acknowledgments

Years from now, I am sure that I will reminisce about my time at Imperial and recall how things were "in the good old days". From my very first day in 'Souwf’ London, where fast friends were made, to my last days on the banks of Fulham before leaving for the Continent, the intervening years have been fondly and indelibly etched in my memory.

Such an attainment could not have been possible without the company and generous help of my friends and colleagues. Many achievements during my sojourn at Imperial were due in large degree to contributions of others, and without whose support the completion of this thesis would not have been possible.

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Abstract

Semiconducting polymers have attracted considerable attention as novel gain materials for laser devices. An important future target in this context is the realisation of a thin-film polymer laser diode. Since inorganic semiconductors are amongst the most important devices in modern optoelectronic technology, there is a lot of interest in achieving electrically pumped laser action in organic semiconductors as a way to broadly tunable lasers covering the whole visible spectrum and producing low-cost laser sources for optical networks.

This thesis reports the results of a study on the design and characterisation of optically pumped blue and violet emitting polymer lasers. The laser devices are based on a range of materials belonging to the polyfluorene family of conjugated polymers which generally show efficient, low threshold stimulated emission. For future electrically pumped polymer lasers, a further reduction of the threshold is crucial since a low threshold fluence directly translates into low current densities.

The optical properties of in total three polyfluorene copolymers are investigated. Lasers based on one of these copolymers are optically-pumped and emission wavelength tuning is demonstrated by altering both grating period and gain polymer thickness, allowing us to cover a part of the spectral region between the blue and ultra-violet that has not been addressed yet by organic semiconductor lasers.

Furthermore, a systematic numerical study of the optical environment on the performance of blue emitting lasers on conducting DFB resonators is presented, which is followed by a demonstration of optically-pumped polymer lasers based on ITO gratings.
Finally, the results of a systematic study into optically pumped blue emitting polymer lasers based on circular Bragg (CBR) resonators is reported. An optimised design strategy is implemented and involves matching the grating profiles with the nulls and maxima from the Bessel functions that represent the radial distribution of the field in a circular resonator.
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<tr>
<td>AFM</td>
<td>Atomic force microscope</td>
</tr>
<tr>
<td>ASE</td>
<td>Amplified spontaneous emission</td>
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<tr>
<td>BN-PFO</td>
<td>2,7-(9,9-dioctylfluorene) repeat units with a 12.7% portion of statistically incorporated 6,6-(2,2-octyloxy-1,1-binaphthyl) groups</td>
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<tr>
<td>CBR</td>
<td>Circular Bragg resonator</td>
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<td>CCD</td>
<td>Charge-coupled device</td>
</tr>
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<td>DFB</td>
<td>Distributed feedback</td>
</tr>
<tr>
<td>F5</td>
<td>9,9-di(2-methyl)butyl fluorene</td>
</tr>
<tr>
<td>F8</td>
<td>9,9-dioctylfluorene</td>
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<tr>
<td>FOP</td>
<td>Poly(9,9-dioctylfluorene-co-(2,5-dioctyloxy)-p-phenylene)</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width at half maximum</td>
</tr>
<tr>
<td>HOMO</td>
<td>Highest occupied molecular orbital</td>
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<tr>
<td>ITO</td>
<td>Indium tin oxide</td>
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<tr>
<td>LEP</td>
<td>Light emitting polymer</td>
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<td>LUMO</td>
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<tr>
<td>Nd:YAG</td>
<td>Neodymium-doped yttrium aluminium garnet; Nd:Y$_3$Al$<em>5$O$</em>{12}$</td>
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<tr>
<td>OLED</td>
<td>Organic light emitting diode</td>
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<tr>
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<td>Personal computer</td>
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<tr>
<td>PFO</td>
<td>Poly(9,9-dioctylfluorene)</td>
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**TCSPC** - Time correlated single photon counting

**THF** - Tetrahydrofuran

**USB** - Universal serial bus

**VASE** - Variable-angle spectroscopic ellipsometry

**Y80F8:20F5** - Statistical copolymer which is made up of 80% 9,9-dioctylfluorene and 20% 9,9-di(2-methyl)butyl fluorene monomer units. Y indicates synthesis by the Yamamoto coupling route.
Chapter 1

Introduction

1.1 Background and Motivation

Back in 1977, Alan J. Heeger, Alan G. MacDiarmid and Hideki Shirakawa discovered that the conductivity of conjugated polymers can be varied across the full range from insulator to metal by chemical redox doping. They were subsequently awarded the Nobel Prize in Chemistry “for the discovery and development of conductive polymers” in the year 2000. Their work helped to initiate the development of a new field of research which includes chemistry, electrical engineering, physics and material sciences. Many well-known companies have started researching organic electronics, which shows the potential of these easily processable materials. The fact that polymers can be deposited as thin films even on flexible substrates, using inexpensive, simple, large-area, low temperature, high-throughput techniques like spin coating, doctor blading, spray coating, as well as gravure, screen or ink jet printing, makes them a commercially very attractive material class.

In recent years, semiconducting (conjugated) polymers have been commercially applied in organic light-emitting diodes for displays$^1$ [1–4] as well as photodetectors$^2$ [5–7], lighting$^3$ [8–10], organic field-effect transistors$^4$ [11–

---

$^1$CDT, Add-Vision Inc., DuPont Displays, Toshiba Mobile Display
$^2$Molecular Vision
$^3$GE, Philips, Osram, BASF, Bosch
$^4$Nano ePrint, Polymer Vision, Plastig Logic, PolyIC
13], and organic solar cells\textsuperscript{5} [14, 15]. However, organic lasers [16–22] and amplifiers [23, 24] are still in the research laboratories. The development of organic light emitting diodes (OLEDs) has been strongly pushed forward by the immense commercial importance of the display market. OLEDs have many advantages over current display technologies (e.g. liquid crystal displays or plasma screens) such as a greater colour gamut and viewing angle, as well as a higher power efficiency and luminance. While liquid crystal displays (LCDs) require a backlight to operate, OLEDs can simply be turned off and thus display deep black levels and draw far less power. Motivated by the rapid progress in organic light emitting diodes, more and more research groups investigated organic lasers. After stimulated emission was demonstrated in organic thin films in the beginning of the 1990s [25], laser emission could be demonstrated some years later [26–28]. Organic lasers have been shown employing a variety of resonator concepts including microcavities [29], microrings [28], microdroplets [30] and distributed feedback (DFB) [31]. However, only optically pumped organic lasers have been demonstrated so far. The development of electrically pumped lasers turned out to be more difficult than assumed for several reasons, mostly relating to the low charge carrier mobilities of the materials [18, 22, 32, 33]. Since the inorganic diode laser is one of the most important devices in modern optoelectronic technology, there is considerable interest in achieving electrically pumped laser action in organic semiconductors as a way to produce broadly tunable lasers covering the whole visible spectrum. So far no reliable report of the fabrication of such a device has been published.

There are four major challenges to this goal:

1. It is difficult to surpass the current densities required to reach laser threshold through most organic semiconductor devices because of their low charge carrier mobilities.

2. Metal layers used for the electrodes introduce additional optical losses

\textsuperscript{5}Konarka, Plextronics, Solarmer, Solar Press
due to absorption and thus raise the threshold even further [34].

3. The low carrier mobility in organic materials leads to much higher charge carrier densities than exciton density. These charges (i.e. polarons) absorb the stimulated emission [35].

4. And finally, it has been shown that singlet-triplet annihilation is a major barrier to electrically-pumped organic lasers [36].

Research in this field is both emphasising the development of improved materials that show strong stimulated emission in combination with good charge carrier properties, as well as the investigation of hybrid concepts [37–39]. In my research, the undertaking was to address the second problem by designing and characterising the optical environment of polymer lasers. The goal was to determine what exactly needs to be considered when designing the architecture of a polymer laser in order to make progress toward a polymer laser device that is feasible for industrial applications.

1.2 Structural Properties of Conjugated Polymers

Semiconducting conjugated polymers are a unique material class for electronic and optoelectronic devices. Their most important advantage is that they combine the easy processability of polymers with the semiconducting properties typical of inorganic semiconductors. In contrast to inorganic semiconductors, organic semiconductors are based on linked carbon chains or rings. The optical and electrical properties of organic semiconductors are due to the $sp^2$-hybridisation of carbon atoms. This will be explained in the rest of this section.
1.2.1 Definitions and Classifications

The word *polymer* is used to describe a macromolecule composed of a large number of repeating units (monomers). These repeating units can either have the same or a different chemical structure. If there is only one type of repeat unit present, the polymer is referred to as *homopolymer*, while polymers containing more than one monomer species are known as *copolymers*. Poly(9,9-dioctylfluorene) (PFO), for example, is composed only of 9,9-dioctylfluorene (F8) units, and is thus classified as a homopolymer. Y80F8:20F5, on the other hand, is composed of 80% F8 and 20% 9,9-di(2-methyl)butyl (F5) units and is thus a copolymer.

Polymers can further be classified based on how these repeating units are configured along the chain. Copolymer types include statistical, alternating and block copolymers. These cases are illustrated in Figure 1.1. Copolymerisation offers a great way to engineer materials with modified properties, such as improved solubility, increased glass transition temperature or higher mobility charge carrier transport.

1.2.2 Molecular Orbitals of Carbon

The electronic configuration of an isolated carbon atom is $1s^22s^22p^2$. The $1s$ and $2s$ orbitals are spherically symmetric, whereas the three different $2p$ orbitals ($2p_x$, $2p_y$, $2p_z$) lie perpendicularly to each other. The two unpaired electrons in the $2p$ orbital would enable the carbon atom to form two bonds. However, when carbon is part of a molecular structure, it can actually form four bonds by mixing its $2s$ and $2p$ orbitals. These orbitals can undergo a hybridisation to form $sp$, $sp^2$ or $sp^3$ orbitals [40]. In total hybridisation ($sp^3$), the $2s$, $2p_x$, $2p_y$ and $2p_z$ orbitals are combined to form a set of four degenerate new hybrid orbitals. These hybrid orbitals are arranged around the nucleus to form a tetrapod. In the partial $sp^2$ hybridisation, three new orbitals of equal energy are formed by the combination of the $2s$ and two
Figure 1.1: Examples of different configurations of repeating units in polymers. Polymers with only one type of repeat unit are referred to as homopolymers. Copolymers consist of a mixture of repeat units which may be organised in a statistical, alternating or block fashion.

Figure 1.2: Energy levels of original and $sp^2$ hybridised orbitals [41].

$2p$ orbitals, while one $2p$ orbital of slightly higher energy, the $p_y$ orbital, for example, remains unaltered as shown in Figure 1.2.

In $sp$ hybridisation, only one $2p$ orbital hybridises with the $2s$ orbital to form two new orbitals, the other two $2p$ orbitals remain unaltered.

In the $sp^2$ hybridised case, the three $sp^2$ orbitals all lie in the same plane,
rotated by 120° with respect to one another. The unaffected \( p_y \) orbital is perpendicular to this plane. This orbital configuration is sketched in Figure 1.3 (b).

Bonding in organic compounds can be explained by the use of valence bond theory and the hybridisation procedure given above. Figure 1.4 shows the bonding diagram of ethylene. A strong sigma bond (\( \sigma \)) is formed by the head-on overlap of \( sp^2 \) orbitals of two carbon atoms along the molecule plane, while the overlap of two \( p_y \) orbitals of adjacent atoms forms a weak \( \pi \) bond, with one lobe above and one below the plane. The remaining two \( sp^2 \) orbitals of each carbon atom overlap with the 1s orbitals of the hydrogen atoms to form further \( \sigma \) bonds. The \( \pi \) bond is weaker than the \( \sigma \) bond because the side-on interaction \( p_y \) orbitals involves less wavefunction overlap. The combination of one \( \pi \) bond and one \( \sigma \) bond between two molecules forms a double bond.

### 1.2.3 Conjugated Polymers

An often-used example to explain the so-called conjugation of polymers is the benzene ring (C\(_6\)H\(_6\)). Three of its valence electrons hybridise to form an \( sp^2 \) orbital. This gives rise to the \( \sigma \) bonds with neighbouring carbon and hydrogen atoms which define the geometry of the molecule. The remaining valence electrons of the \( p_y \) orbitals are aligned perpendicularly to the plane of
Figure 1.4: Formation of a $\sigma$ bond through an end-to-end overlap of two $sp^2$ orbitals (violet), and a $\pi$ bond through a side-on overlap of two adjacent $p_y$ orbitals [42].

![Diagram of ethylene with $\sigma$ and $\pi$ bonds](image)

Figure 1.5: Benzene ring: (a) chemical structure, (b) distribution of $\sigma$ orbitals, (c) distribution of $\pi$ orbitals [44].

![Image of benzene ring with $\sigma$ and $\pi$ distributions](image)

The $\sigma$ orbitals. Figure 1.5 shows the chemical structure of a benzene ring, as well as its $p_y$ and $sp^2$ orbitals. The wavefunctions of the $p_y$ orbitals overlap around the ring, forming $\pi$ bonds with neighbouring carbon atoms. The result is an alternating single and double bond structure. This process of dimerisation is also called conjugation. In this so-called conjugated $\pi$ system, the electrons are no longer localised at a single C-C bond but of a delocalised nature [43].

Similar to benzene, conjugated polymers have a backbone of alternating single ($\sigma$) and double bonds ($\sigma+\pi$). They consist of strong $\sigma$ bonds and a network of $\pi$ bonds containing delocalised $\pi$ electrons. However, the delocalisation of the $\pi$ electrons along the chain is disrupted by defects like torsions, kinks or chemical impurities in real materials. For this reason, a polymer
material behaves like an accumulation of short π conjugated segments with a typical length of 5 to 10 units (conjugation length) \[45\]. These segments can also be considered chromophores and determine the optical properties of the polymer. An explanation of chromophores will be given in Section 1.3.2.

The conductivity of organic semiconductors is based on the presence of delocalised π electrons. We assume two isolated atoms A and B with the normalised ground state wavefunction \[46\] (here for atom A):

\[
\Psi = \Psi_s(r_A)
\]  

(1.1)

When these atoms are brought together, there respective electrons can simultaneously experience a strong attraction to both nuclei. As the wavefunction must be symmetrical about the centre between the two nuclei, the following linear combinations are possible \[47\]

\[
\Psi_g = \frac{1}{\sqrt{2}} [\Psi_s(r_A) + \Psi_s(r_B)],
\]  

(1.2)

\[
\Psi_u = \frac{1}{\sqrt{2}} [\Psi_s(r_A) - \Psi_s(r_B)].
\]  

(1.3)

Here \(r_A\) and \(r_B\) are the distances of the electron to each of the two nuclei, \(\Psi_g\) is the even (gerade) solution and \(\Psi_u\) is the odd (ungerade) solution. So, two new molecular orbitals are formed. The probability density \(|\Psi_u|^2\) of the odd wavefunction has a null between the nuclei, which means that the electron rarely is at this position. Consequently, it keeps the nuclei less together than in the even solution. The \(\Psi_g\) orbital is therefore referred to as the π or bonding orbital and the \(\Psi_u\) orbital is called the π* or antibonding orbital.

An electron in the π* orbital has a higher potential energy than one in the π orbital, with the effect that the π* orbital is the lowest unoccupied molecular orbital (LUMO), while the π orbital is the highest occupied molecular orbital (HOMO). These orbitals correspond to valence and conduction bands in inorganic semiconductors. Transitions between HOMO and LUMO are commonly referred to as \(\pi \rightarrow \pi^*\) transitions.
The Coulomb interaction between a hole (which is the absence of an electron) in the HOMO and an electron in the LUMO leads to a bound state which is referred to as exciton. Depending on the relative spin of the electron and the hole, an exciton can be either in the singlet state $S_n$, with antiparallel spin orientations, or in the triplet state $T_n$, with parallel spin orientations.

1.3 Optical Properties of Conjugated Polymers

1.3.1 Photoexcitations and Optical Transitions

The variety of photophysical processes that can occur following the absorption of a photon in a conjugated polymer is illustrated by the Jablonski diagram in Figure 1.6, which depicts the electronic states of a polymer vertically, and the spin multiplicity horizontally [48]. As indicated, the electronic states $S_0, S_1, S_2, T_1...$ consist of vibrational levels. Electronic downward transitions are divided into radiative transitions under emission of a phonon and nonradiative decays. If a photon is absorbed (duration $\sim 10^{-15}$ s), the energy excites an electron into a higher singlet state $S_0, \nu \rightarrow S_n, \nu'$. A triplet-absorption from the ground state $S_0, \nu=0$ is strongly forbidden as it would require a change in the spin, which would infringe spin angular momentum conservation [49]. After excitation, the molecule relaxes to the lowest vibrational level of its electronic level, giving off its excess energy in form of heat. It then emits a photon at a longer wavelength, either by a spontaneous or stimulated emission process. This process is known as fluorescence $S_1, \nu' \rightarrow S_0, \nu$. Besides the excitation by an absorbed photon (photoexcitation), excitations by the recombination of injected charge carriers are possible. In this case, the emitted radiation is called electroluminescence.

The excited singlet $S_1, \nu'$ can also decay non-radiatively $S_1, \nu' \rightarrow S_0, \nu$
Figure 1.6: Jablonski diagram illustrating the electronic and vibronic states of a conjugated polymer with singlet and triplet systems. Main photophysical processes are categorised into absorption (red solid lines), emission (yellow solid lines), nonradiative decays and relaxation (violet dashed lines) and intersystem crossing (green dashed lines). After [43].

or undergo an intersystem crossing and be transferred by a radiationless process into a triplet state $S_1, \nu' \rightarrow T_1, \nu'$. From there, it can decay nonradiatively $T_1, \nu' \rightarrow S_0, \nu$ or undergo the spin-forbidden emission of a photon $T_1, \nu' \rightarrow S_0, \nu$. The resulting radiation is called phosphorescence.

Fluorescence has a high transition probability and hence short lifetimes in the range of $10^{-9}$ to $10^{-6}$ s. In contrast, typical phosphorescence lifetimes range from $10^{-3}$ to $10^2$ s. However, the probability of these transitions is three to five orders of magnitude lower compared to $S_1, \nu' \rightarrow S_0, \nu$ transitions [50]. As a consequence of this, excited triplet states play no important role in stimulated processes.
1.3.2 Optical Absorption and Photoluminescence

The nuclei of a molecule are bound together elastically by covalent bonds and can therefore perform vibrations around the equilibrium position. When excited, the bonding forces between the nuclei are usually different from those in the ground state. As a consequence, the nuclei in excited states vibrate around different equilibrium positions. Figure 1.7 sketches the potential energy surface as a function of a nuclear coordinate $R$ for the lowest singlet state and the ground state, each with several vibrational levels ($\nu$ and $\nu'$).

Since electronic transitions (absorption and emission) take place on a much faster timescale than periods of nuclear vibrations ($\sim 10^{-15}$ s compared to $\sim 10^{-12}$ s), the Born-Oppenheimer approximation can be applied during absorption and emission processes. It states that nuclei can be treated as being stationary since they move so slowly relative to electrons. According to the Franck-Condon principle all electronic transitions in Figure 1.7 can therefore be plotted vertically.

Due to the large vibronic quantum energy of $\sim 0.15$ eV, a molecule at room temperature occupies the lowest vibrational ground state $S_0, \nu = 0$ (c.f. $kT$ at room temperature is $\sim 0.025$ eV). Absorption of a photon of suitable energy leads to a $S_0, \nu = 0 \rightarrow S_1, \nu' = n$ vibronic transition. The transition probability is determined by the overlap integral of the wave functions of both ground and excited state. Absorption is followed by relaxation into the lowest vibrational level $\nu' = 0$ of the $S_1$ state by internal conversion, from which a radiative transition can then take place into any of the vibrational levels of $S_0$ (again with probability determined by the associated overlap integrals).

The emission wavelength is therefore a function of the energy difference of this radiative transition. If the energy difference of a particular spatial region of a polymer falls within the visible spectrum (1.59 to 3.18 eV), this region is called a chromophore.

The spectra given in Figure 1.7 address an important observation, namely
Figure 1.7: Potential energy surface as a function of nuclear coordinate R. Vibronic eigenstates are denoted by \( \nu \) and \( \nu' \). The vibronic transitions are indicated by upward (absorption) and downward (emission) arrows. Corresponding absorption and luminescence spectra are shown below. After [51].

the shift towards lower energies of the emission in relation to the absorption spectrum. This difference between the absorption and emission maxima is known as a Stokes shift. For an isolated molecule, it is due to the exciton losing energy by excitation of phonons (local vibrations) before it decays [52].

In the field of OLEDs and lasers, the Stokes shift is of much interest, since it minimizes the re-absorption of emitted photons and thus increases efficiency.

Although, the figure suggests mirror image symmetry around \( E_0 \), this is generally not the case for conjugated polymers. The reason for this is the wide range of conjugation lengths within a given sample. According to

---

6Phonons in crystalline materials strictly have an extended wavefunction and band of states with a dispersion relation. In molecules, the vibrations are localised spatially, i.e. are not represented by a band structure.
the simple idealised model of a particle in a box, the energy of an exciton will be lower, the longer the conjugated segment within which it sits is. Additionally, the conjugated segments experience a high degree of disorder in their local environment. This leads to a Gaussian distribution of the HOMO and LUMO energies [53], which are all sampled during absorption processes. On the other hand the lifetime of the excitons allows them to diffuse to lower energy sites before emission. Hence, the vibronic structure of polymers is seen more clearly in emission than in absorption spectra.

1.3.3 Quenching Mechanisms

As previously mentioned in Section 1.3.1, not every excitation leads to a singlet exciton that decays via the emission of a photon. There are several mechanisms that compete with radiative decay. These include intersystem crossing which leads to the population of triplet states which do not contribute to stimulated emission and various exciton quenching processes such as bimolecular singlet-singlet annihilation, singlet-triplet annihilation, singlet-polaron/bipolaron quenching, singlet decay at chemical defects and impurities and so on [54].

Singlet-singlet annihilation describes a process in which a singlet exciton recombines and transfers its energy to a second singlet exciton, exciting it to a higher state. From there, it can either relax into the first exited singlet or triplet state.

In singlet-triplet annihilation, the recombining singlet exciton raises a triplet exciton into a higher triplet state. It then quickly relaxes into the first excited triplet state.

Singlet excitons can also be quenched by polarons or bipolarons. Here, the energy of the exciton is transferred to an electron or a hole, which is excited to a higher lying charge state. The polaron/bipolaron is not removed by this process and can therefore quench many excitons.
In the past, it has been assumed that a polymer laser diode will basically work on the same principles as an OLED. Therefore, much interest and research effort was put into enhancing the emission efficiency of conjugated polymers, and at the time of writing this, the photoluminescence quantum efficiency (PLQE) even of blue emission polymers can be as high as 75% [55]. However, there is increasing evidence that high PLQE values are not necessarily any guarantee of achieving lasing [56].

Another issue related to triplet states is that they can sensitise the formation of highly reactive singlet oxygen - the ground state of molecular oxygen is a triplet and can therefore efficiently extract excitation energy from other triplet states. Singlet oxygen is a major concern for oxidative stability.

1.4 Thesis Outline

In Chapter 2, the theory of distributed feedback polymer lasers upon which this thesis relies is established. A brief introduction into optical amplification and waveguides is provided, and the fundamental principles of laser oscillation are described. Finally, based on the theory of distributed feedback (DFB), the operation method and design of the resonators employed throughout this thesis are presented.

Chapter 3 deals with aspects of the techniques and methodology used throughout this thesis, describes the preparation of samples as well as the measurement of absorption, fluorescence and lasing, and presents some considerations about the optimisation of amplified spontaneous emission (ASE) measurements. Finally, it presents the results of a study of the optical properties of poly(9,9-dioctyl-fluorene-co-(2,5-dioctyloxy)-p-phenylene) (FOP); BN-PFO, a copolymer which consists of 2,7-(9,9-dioctylfluorene) repeat units and a minor portion of statistically incorporated 6,6-(2,2-octyloxy-1,1-binaphthyl) groups; and a statistical copolymer which is made up of 80% 9,9-dioctylfluorene and 20% 9,9-di(2-methyl)butyl side chains (Y80F8:20F5).
The subjects of Chapter 4 are lasers based on the copolymer FOP for violet and blue light emission. It is shown that the emission wavelength of laser devices based on these polymers span the range from 418.9 to 447.1 nm, establishing a spectral region that was previously unaddressed with conjugated polymer gain materials.

In Chapter 5, the design and characterisation of multi-layer structures is presented. Design considerations for a most favourable device architecture are given in order to minimise losses arising from contact layers, while maintaining light emitting polymer (LEP) films of realistic thickness. Transfer matrix calculations for TE and TM waveguide mode profiles in a multi-layer structure are used to optimise the device parameters accordingly to the desired architecture. The fabrication of devices based on DFB resonators written into indium tin oxide (ITO) is described. And finally, the results of laser experiments on ITO and SiO$_2$ gratings are reported.

Chapter 6 follows the logical progression laid down in Chapter 2.7 and concerns the demonstration of circular Bragg resonators as a way to reduce the threshold energy for laser oscillation, improve the output beam, and increase the Q-factor of polymer lasers. High Q, low-threshold, single mode lasing is achieved under optical excitation. The devices, using both BN-PFO and Y80F8:20F5 as gain media, are the first blue emitting circular grating semiconductor lasers (either organic or inorganic). They exhibit feature sizes as small as 47 nm and emit azimuthally polarised beams. A detailed study shows the influence of the grating parameters on the laser characteristics. The modal properties of the output beam in dependence of both excitation localisation and intensity are measured and correlated with the lasing modes.

In Chapter 7, a synopsis of the thesis is given and the long term outlook for polymer laser diodes is considered. Some suggestions for future work are discussed.
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Chapter 2

Principles of Distributed Feedback Polymer Lasers

2.1 Introduction

The term *laser* stands for “light amplification by stimulated emission of radiation” and its development is at least as interesting as its theory. The beginning of laser theory is commonly attributed to Einstein’s postulation of stimulated emission which was published 1916 in the essay *Zur Quantentheorie der Strahlung* [1]. However, he did not name this process. The first experimental proof of stimulated emission in neon gas discharges was demonstrated 1928 by Kopfermann and Ladenburg [2]. They, however, did not call it *stimulated emission* but *negative dispersion*. In 1954 and 1955, the next big step was taken when Gordon et al. presented a device for the amplification of microwaves which they called a *maser* (“microwave amplification by stimulated emission of radiation”) [3, 4]. With a working maser, thoughts came up for the development of an optical maser. This device was first theoretically treated by Schawlow and Townes in 1958 [5], and then experimentally demonstrated by Maiman in 1960 [6].

Since then, the development of laser devices and their applications has been phenomenal. Today, lasers can be found in every aspect of life, ranging from semiconductor lasers in laser pointer and DVD players, to CO$_2$ lasers...
used in industrial laser cutting. One laser type of particular interest in this thesis is the semiconductor laser based distributed feedback (DFB) laser which was demonstrated in 1971 by the two Bell Labs researchers, Kogelnik and Shank [7]. DFB lasers offered the advantages of having a very narrow linewidth, a modulation capability of gigabit/s [8], compact manufacturability and the possibility of wavelength tuning, and have thus lead to extensive optical fibre communication networks over the last decades.

As it was made clear in Chapter 1, conjugated polymers are promising gain media for the application in novel measurement and information technology devices. These could rely on large area emitters which are not achievable with conventional semiconductor lasers. Research in the field of organic semiconductor lasers is to a great extent driven by the endeavour to realise polymer laser diodes.

The following sections will discuss the three different processes of interaction between light and matter - absorption, spontaneous emission and stimulated emission. The fundamental theory of laser oscillation will be covered as well as optical waveguides. Finally, the principles of DFB lasing and some more complex DFB resonator designs will be explained.

2.2 Spontaneous and Stimulated Emission

We consider an assembly of molecules and describe them as a four-level system at room temperature [9]. We define the energy of the ground state as $E_0$, that of the lower laser level as $E_1$, of the upper laser level as $E_2$ and that of the pump level as $E_3$. In accordance with Figure 1.7, $E_0$ is the energy of ground state $S_0, \nu=0$, $E_1$ is the energy of a higher vibronic eigenstate $S_0, \nu=n$, $E_2$ is the lowest vibrational level of the first excited electronic state $S_1, \nu'=0$, and $E_3$ is the energy of a higher vibrational level $S_1, \nu'=n$. If we assume that $E_1 - E_0 >> kT$, nearly all electrons can be found in the ground state $E_0$. If energy of at least $\hbar c/\lambda = E_2 - E_0$ is applied to the molecules,
the \( \pi \) electrons will be excited or pumped into excited energy states. This process can happen in the form of electric current or light absorption, and is known as induced absorption. The probability \( W_{03} \) of an electron to undergo a \( S_0, \nu=0 \rightarrow S_1, \nu'=n \) transition per time \( dt \) can be described in terms of the Einstein coefficient for absorption \( B_{03} \) \(^{[10]}\)

\[
dW_{03} = u(\lambda)B_{03}dt, \tag{2.1}
\]

where \( u(\lambda) \) is the photon energy density at wavelength \( \lambda \). Thus, the transition rate for absorption is proportional to \( u(\lambda) \). If \( N_0 \) is the population density of ground level \( E_0 \),

\[
dN_{03} = N_0dW_{03} = N_0u(\lambda)B_{03}dt \tag{2.2}
\]
electrons will be excited to pump level \( E_3 \) during time \( dt \).

The electrons then relax very quickly into the upper laser level \( E_2 \), and after an average lifetime \( \tau_{sp} \) in level \( E_2 \), they decay spontaneously into the lower laser level \( E_1 \) without external influences. This transition can be accompanied by the emission of a photon at wavelength \( \lambda \), according to Planck’s relation

\[
E_2 - E_1 = \frac{hc}{\lambda}. \tag{2.3}
\]

Non-radiative transitions are also possible but shall not be discussed here. The emission direction and polarisation of spontaneously emitted photons is random. For this reason, spontaneous emission creates incoherent radiation.

The transition probability \( W_{21} \) of an electron to undergo a transition from level \( E_2 \) to level \( E_1 \) during the period \( dt \) can be described by the Einstein coefficient for spontaneous emission \( A_{21} \)

\[
dW_{21} = A_{21}dt \tag{2.4}
\]
with

\[ A_{21} = \frac{1}{\tau_{sp}}. \] (2.5)

The change of population density \( N_2 \) of the upper laser level due to spontaneous emission is then given by

\[ dN_{21} = -N_2 dW_{21} = -N_2 A_{21} dt. \] (2.6)

A downward transition of an electron from \( E_2 \) to \( E_1 \) can also be caused by an incident photon. This process is called stimulated emission. The emitted photon has the same energy, phase and direction as the incident one. The fact that an additional photon of same properties is released means that there has been amplification of the incident photon. The corresponding transition probability \( dW_{21} \) can be described by the Einstein coefficient for stimulated emission \( B_{21} \)

\[ d\dot{W}_{21} = u(\lambda) B_{21} dt. \] (2.7)

Like induced absorption, it is proportional to the photon energy density \( u(\lambda) \) of the incident radiation. Per period \( dt \),

\[ d\dot{N}_{21} = N_2 d\dot{W}_{21} = N_2 u(\lambda) B_{21} dt \] (2.8)

electrons perform a transition to the lower laser level \( E_1 \) by stimulated emission from where they, after a very short time of only a few picoseconds, relaxate back into the ground level \( E_0 \). Figure 2.1 summarises the absorption and emission processes in a four-level system and can be considered as a simplified scheme of the Jablonski diagram in Figure 1.6.
2.3 Rate Equations

We consider an ideal four-level system such as the one shown in Figure 2.1. The population density \( N_0 \) of the ground state \( E_0 \) is decreased by a pumping process into the pump level \( E_3 \) and increased by very fast relaxation from the lower laser level \( E_1 \). The population density \( N_1 \) of energy \( E_1 \) is decreased by the relaxation process into the ground level and increased by spontaneous as well as stimulated emission. According to this, the population density \( N_2 \) of the higher laser level \( E_2 \) is decreased by spontaneous and stimulated emission and increased by a very fast relaxation process from the pump level \( E_3 \). Thus, the equations

\[
\frac{dN_0}{dt} = -u(\lambda)\sigma_p N_0 + k_{10} N_1, \tag{2.9}
\]

\[
\frac{dN_1}{dt} = \frac{N_2}{\tau_{sp}} + B_{21} S (N_2 - N_1) - k_{10} N_1, \tag{2.10}
\]

\[
\frac{dN_2}{dt} = k_{32} N_3 - \frac{N_2}{\tau_{sp}} - B_{21} S (N_2 - N_1), \tag{2.11}
\]
\[
\frac{dN_3}{dt} = u(\lambda)\sigma_p N_0 - k_{32} N_3,
\]  \hspace{1cm} (2.12)

describe the interaction between an incident radiation field and the four-level system. Here, \( N_i \) represent the level population densities \((i = 1, 2, 3, 4)\), \( \sigma_p \) is the absorption cross-section at the wavelength of the pump, \( k_{ij} \) are the relaxation rates from the \( i \) to the \( j \) energy levels, \( \tau_{sp} \) is the lifetime of the energy level \( E_2 \) and \( S \) is the photon density.

Up to now, we did not consider this photon density \( S \) which is of course an important quantity for the description for a laser. It determines whether the radiation field is amplified or not. The photon density is given by

\[
\frac{dS}{dt} = \Gamma B_{21} S (N_2 - N_1) + \Gamma \beta \frac{N_2}{\tau_R} - \Gamma \frac{S}{\tau_{ph}},
\]  \hspace{1cm} (2.13)

where \( \Gamma \) is the mode confinement, \( \beta \) is the spontaneous emission factor and gives a measure of the fraction of light that propagates in the considered mode, \( \tau_R \) is the radiative lifetime of \( N_2 \), and \( \tau_{ph} \) is the photon lifetime. For amplification, the photon density has to grow, i.e.

\[
\frac{dS}{dt} > 0,
\]  \hspace{1cm} (2.14)

which is the case for

\[
N_2 \left( B_{21} + \frac{\beta}{\tau_R S} \right) > N_1 B_{21} + \frac{1}{\tau_{ph}}.
\]  \hspace{1cm} (2.15)

The sufficient condition for amplification is a higher population of the upper laser level compared to the lower one. This situation is called population inversion and is either achieved by optical, electrical or chemical excitation. The net stimulated absorption and emission-transition rate is then in the downward direction.
2.4 Amplified Spontaneous Emission

Spectral gain narrowing in conjugated polymers was first observed by Hide et al. using a MEH-PPV film that contained scattering TiO$_2$ nanoparticles [11]. The reason for this phenomenon can be deduced from equations (2.4) and (2.7) which show that the photon energy density, $u(\lambda)$, determines the transition probability of stimulated but not of spontaneous emission. If the excitation intensity is increased to that point where stimulated emission outweighs spontaneous emission, the emission spectrum will be dominated by amplified spontaneous emission (ASE). The theory of ASE is based on a one-dimensional approximation describing the rate of change of fluorescence as a function of the pumped region [12, 13]. When the excitation energy is high enough to obtain net gain in the polymer, spontaneously emitted photons that happen to be directed along the pumped region (i.e. the region of population inversion) can stimulate the emission of further photons. Since optical gain $g(\lambda)$ is a function of the wavelength, the spectral region around the peak gain experiences the highest amplification. The net gain’s dependence on the wavelength leads to significant spectral narrowing of the emission [11, 14–19]. Typical ASE full width at half maximum (FWHM) range from 4 to 10 nm.

We now consider the change of fluorescence with respect to the length of the pumped region. Light with intensity $I$ is propagating through the gain medium (here along the $z$ axis). At the end of the medium, the amplified light intensity due to stimulated emission is

$$\frac{dI(\lambda)}{dz} = g_{net}(\lambda) I(\lambda),$$

(2.16)

where $g_{net}$ is the net gain per length (gain minus loss). The intensity due to spontaneous emission is

$$\frac{dI(\lambda)}{dz} = \frac{A_{21} N_2 hc}{\lambda} \frac{A}{4\pi L^2},$$

(2.17)
where \( A \) is the cross-sectional area of the gain medium, and \( L \) is the length of the gain medium. Note that the factor \( \frac{A}{4\pi L^2} \) describes the fraction of a considered solid angle since only a small fraction of the photons is emitted into the \( z \) direction. Taking both stimulated and spontaneous emission into account leads to

\[
\frac{dI(\lambda)}{dz} = g_{\text{net}}(\lambda)I(\lambda) + \frac{A_21N_2hc}{\lambda} \frac{A}{4\pi L^2}.
\] (2.18)

The solution of this equation is

\[
I(\lambda, z) = \frac{A_21N_2hc}{\lambda g_{\text{net}}(\lambda)} \frac{A}{4\pi L^2} \left( e^{g_{\text{net}}(\lambda)z} - 1 \right).
\] (2.19)

ASE is therefore exponentially dependent on the length of the amplifying medium.

### 2.5 Optical Waveguides

Over the last two decades, advances in data transmission have revolutionised the speed with which we perform communications of all kinds. High bandwidth datacom and telecom can be realised through guided-wave optics. Optical waveguides may be used in the form of thin-film optoelectronic devices, integrated optical circuits, or in fibre optics. And although the basic design of many integrated optical circuits is already in place, the industry has as yet no clear favourite material. However, polymers are expected to outperform alternative materials in growth [20].

In this section, a brief introduction into wave equations is given and the fundamental theory of optical waveguides is presented.

#### 2.5.1 The Wave Equation and Plane Waves

All equations in this thesis that deal with electromagnetism are derived from the laws which in their mathematical expression are known as Maxwell’s
equations \[9\],

\[
\nabla \times \mathbf{E} + \frac{\partial \mathbf{B}}{\partial t} = 0, \tag{2.20}
\]

\[
\nabla \times \mathbf{H} - \frac{\partial \mathbf{D}}{\partial t} = \mathbf{J}, \tag{2.21}
\]

\[
\nabla \cdot \mathbf{D} = \rho, \tag{2.22}
\]

\[
\nabla \cdot \mathbf{B} = 0, \tag{2.23}
\]

where \( \mathbf{E} \) and \( \mathbf{H} \) are the electric field vector and magnetic field vector. \( \mathbf{D} \) is the electric displacement vector, and \( \mathbf{B} \) is the magnetic induction vector. The remaining quantities \( \rho \) and \( \mathbf{J} \) are the electric charge density and electric current density vector, respectively. To solve Maxwell’s equations, they have to be supplemented by the constitutive relations between \( \mathbf{D} \) and \( \mathbf{E} \), and \( \mathbf{B} \) and \( \mathbf{H} \):

\[
\mathbf{D} = \varepsilon \mathbf{E}, \tag{2.24}
\]

\[
\mathbf{B} = \mu \mathbf{H}, \tag{2.25}
\]

where \( \varepsilon \) and \( \mu \) are scalar constants and known as the permittivity and permeability, respectively.

To derive the wave equations, we assume that there are no free charges \((\rho = 0)\) and no current \((\mathbf{J} = 0)\). Taking the curl of equations (2.20) and (2.21), and using equations (2.22) to (2.25), we obtain (full details are given in the appendix)

\[
\nabla^2 \mathbf{E} - \mu \varepsilon \frac{\partial^2}{\partial t^2} \mathbf{E} = 0. \tag{2.26}
\]

The corresponding equation for the magnetic field vector can be written as

\[
\nabla^2 \mathbf{H} - \mu \varepsilon \frac{\partial^2}{\partial t^2} \mathbf{H} = 0. \tag{2.27}
\]

For this thesis, we can limit these wave equations to monochromatic solutions. By separating the time dependence of the electric or magnetic field from its amplitude in the product \( \mathbf{E}(\mathbf{r},t) = \mathbf{E}(\mathbf{r})e^{i\omega t} \), \( \mathbf{H}(\mathbf{r},t) = \mathbf{H}(\mathbf{r})e^{i\omega t} \).
respectively and using the respective equations (2.26) and (2.27), we obtain

\[ \nabla^2 E(r) + \mu \varepsilon \omega^2 E(r) = 0, \quad (2.28) \]

\[ \nabla^2 H(r) + \mu \varepsilon \omega^2 H(r) = 0, \quad (2.29) \]

where \( \mu \varepsilon \omega^2 = k_0^2 n^2 \), with the angular frequency \( \omega \), the refractive index \( n \), and the wavenumber \( k_0 \). Using the complex formalism, the solutions of equation (2.28) and (2.29) can be written in the forms [9]

\[ E = E_0 e^{i(\omega t - k_0 n r)}, \quad (2.30) \]

\[ H = H_0 e^{i(\omega t - k_0 n r)}. \quad (2.31) \]

Waves of such a nature are referred to as plane waves because, at any given moment, each point with \( r = \text{constant} \) (a plane) has the same phase. This plane is often called a wavefront.

### 2.5.2 The Basic Waveguiding Structure

Polymer waveguides consist of planar thin-films deposited on a substrate. The simplest example is a three layer waveguide. Polymer waveguide structures are normally asymmetric since \( n_a < n_s < n_p \), where \( n_a \), \( n_s \) and \( n_p \) are the refractive indices of air, the substrate and the polymer respectively.

To guide waves (or modes), the core refractive index of the waveguide (here \( n_p \)) has to be of a larger value than the others [21]. In waveguides the axial guiding of light is achieved by a discrete variation of the refractive index perpendicular to the \( z \) axis direction. Hence, there is no variation in the \( y \) direction, but in the \( x \) direction. In this case the total internal reflection of light at the inner interface of planar slab waveguides causes the waveguiding effect. Figure 2.2 shows the schematic setup of an asymmetric waveguide.

We assume propagation along the \( +z \) axis. The general plane wave solution
Figure 2.2: Schematic of a simple asymmetric slab waveguide. Plane waves propagating under an angle $\theta$ are totally reflected at the interfaces and waveguided in the polymer layer. For TE polarised waves, the electric field vector points in $y$ direction and thus has the field components $E_y$, $H_x$ and $H_z$. For TM polarised waves, the magnetic field vector points in direction. The field components are $H_y$, $E_x$ and $E_z$. 

in equation (2.30) becomes

$$E(x, y, z) = E(x, y)e^{-i\beta z}$$

(2.32)

where $\beta$ is referred to as the propagation constant. Since there is no variation in the $y$ direction, we can set $\frac{\partial}{\partial y} = 0$, and insert (2.32) into (2.28), to get [9]

$$\frac{\partial^2}{\partial x^2}E(x, y) + (k_0^2n_i^2 - \beta^2)E(x, y) = 0.$$  

(2.33)

This equation is valid for each of the three layers ($n_s$, $n_p$ and $n_a$). There exist two polarisations for the slab waveguide which can be classified as either transverse electric (TE) or transverse magnetic (TM) modes. In case of the TE mode, the electric field vector points in the $y$ direction and thus has only the field components $E_y$, $H_x$ and $H_z$. The second case is characterised by vanishing $H_x$. The TM mode has therefore the field components $H_y$, $E_x$ and $E_z$. The rest of this thesis will focus more on TE modes since TM modes
usually have a weaker confinement in the gain material and hence would overlap more strongly with electrodes of the device, which leads to higher absorption losses. More on this issue can be found in Chapter 5.

The relevant angle for total internal reflection is

\[ \theta_{\text{critical}} = \arcsin \left( \frac{n_s}{n_p} \right). \] (2.34)

Therefore, as mentioned before, the waveguide requires a maximum of the refractive index in the polymer. We assume that light propagates along the \( z \) direction. This light has the wavelength \( \lambda \), and propagates with the wavevector \( k_0 n_p \), where \( k_0 \) is [22]

\[ k_0 = \frac{2\pi}{\lambda n_{\text{eff}}} = \frac{2\pi}{\lambda n_p \sin(\theta)}, \] (2.35)

where \( n_{\text{eff}} \) is the effective refractive index. Light propagates through these waveguides only in certain modes. It is therefore sufficient to focus on the so-called self-consistency condition for a guided mode in asymmetric waveguides. For a three layer waveguide this self-consistency condition is given by [23]

\[ 2k_0 n_p d \cos \theta = 2\varphi_a + 2\varphi_s + 2m\pi, \] (2.36)

where \( d \) is the polymer film-thickness, \( \theta \) is the propagation angle, \( \varphi_a \) and \( \varphi_s \) are the phase shifts due to total reflection from the polymer-air and polymer-substrate interfaces, and \( m \) is an integer (\( m = 0, 1, 2, \ldots \)) which identifies the mode number. According to the equation above, not all mode propagation angles \( \theta \) are allowed but only a discreet set of angles. The phase shifts \( \varphi_a \) and \( \varphi_s \) are functions of \( \theta \) and can be written as [23]

\[ \varphi_a = \arctan \left( \frac{\sqrt{n_p^2 \sin^2 \theta - n_a^2}}{n_p \cos \theta} \right), \] (2.37)
Figure 2.3: Simulation of the self-consistency condition for the fundamental guided TE mode at $\lambda = 450$ nm for different gain polymer layer thicknesses. Blue lines indicate left part and orange line indicates right part of equation (2.36). The model is based on an asymmetric polymer waveguide (with $n_a = 1.0$, $n_p = 1.96$ and $n_s = 1.46$).

$$\varphi_s = \arctan \left( \frac{\sqrt{n_p^2 \sin^2 \theta - n_s^2}}{n_p \cos \theta} \right).$$  \hspace{1cm} (2.38)

To illustrate the meaning of equation (2.36), some simulation results for the TE$_0$ mode at $\lambda = 450$ nm are shown in Figure 2.3. The model was based on an asymmetric slab waveguide with refractive indices $n_a = 1$, $n_p = 1.96$ and $n_s = 1.46$. The blue curves symbolise the left part $(2k n_p d \cos \theta)$ of equation (2.36) for five different polymer layer thicknesses. The orange curve is a plot of the phase sum of the right part of the self-consistency equation. The intersections of both curves are solutions of the self-consistency equation and the corresponding angles identify the propagation angles of the TE$_0$ mode in respect to the polymer surface.

### 2.6 Laser Oscillation

In general, a laser consists of an amplifying material (gain medium) placed in a resonant cavity that provides feedback. For a laser to operate, the gain
medium is usually pumped by a light source (for example a flashlamp or another laser) or electrically. The intensity $I$ of the light in the cavity varies with distance as in

$$I(z) = I_0 e^{g_{\text{net}}(\lambda) z}, \quad (2.39)$$

where $g_{\text{net}}(\lambda)$ is the net gain coefficient. Since gain saturates for high intensities [24], this is only correct for small intensities. Consequently, $g_{\text{net}}(\lambda)$ is also called small signal gain. Of course, loss processes due to scattering or absorption also take place in a laser. These losses can be described by the waveguide loss coefficient $a_{\text{wg}}(\lambda)$. With $a_{\text{wg}}(\lambda)$, equation (2.39) can be written as

$$I(z) = I_0 e^{[\Gamma_p g(\lambda) - a_{\text{wg}}(\lambda)] z}, \quad (2.40)$$

where $g(\lambda)$ is the material gain coefficient and $\Gamma_p$ the confinement factor in the gain polymer. As can be seen, light is only amplified for positive net gain coefficients, and increases exponentially with net gain and propagation length. The material gain is given by the product of the wavelength dependent cross section for stimulated emission $\sigma_{\text{se}}$ and the volume density difference of states $N_2 - N_1$ [25]. The spectral dependence of the gain coefficient $g(\lambda)$ is determined by the spectral dependence of $\sigma_{\text{se}}$, which is in most cases very similar to the photoluminescence spectrum of the polymer [26] and given by

$$g(\lambda) = \sigma_{\text{se}}(\lambda) (N_2 - N_1), \quad (2.41)$$

and [10, 27]

$$\sigma_{\text{se}}(\lambda) = \frac{\hbar}{c\lambda (\lambda_1^{-1} - \lambda_2^{-1})} B_{21}, \quad (2.42)$$

where $c$ is the speed of light, $\lambda$ is the laser wavelength, and $\lambda_1$ and $\lambda_2$ are the shorter and longer wavelengths at full width at half maximum (FWHM) of the laser line. $B_{21}$ is the Einstein coefficient for stimulated emission used in the rate equations.

Adding a resonant cavity is the final step necessary for laser oscillation. Several different resonator architectures can be used to introduce feedback in
polymer lasers. In the classic case of a Fabry-Perot resonator, two opposing parallel mirrors provide highly reflective feedback while the gain medium is situated in-between. If the net round-trip gain of the plane wave in the cavity is less than zero, the intensity decreases during each pass through the resonator and only spontaneous emission can be observed. However, the intensity increases exponentially if after each round-trip the gain minus loss is greater than zero. In this case, laser oscillation can be observed. The point at which the gain is equal to losses is called laser threshold. It corresponds to a well defined pump energy. This concept of net round-trip gain holds for all resonator architectures, not just for Fabry-Perot lasers.

2.7 Distributed Feedback Structures

Among the various structures that are used to provide resonant feedback [10, 24, 25], the concept of distributed feedback (DFB) has proven to be the most satisfying architecture in terms of strong feedback and long propagation lengths [28]. In DFB resonators, feedback is provided by backward Bragg scattering from periodic structures. The first DFB laser was demonstrated in 1971 by Kogelnik and Shank using gelatine films in which Rhodamine 6G was dissolved [7]. The first DFB semiconductor laser was realised two years later by Nakamura et al. [29]. Nowadays, electrically-pumped DFB lasers and are extensively used with inorganic materials [30], covering a wide range of applications, the most important being the telecommunication sector. What makes the DFB resonator so attractive for polymer lasers is that fact these periodic structures can be readily incorporated into planar conjugated polymer waveguides and do not need good-quality end facets to provide feedback. The laser therefore consists of a thin polymer (or small molecules) film deposited on top of a corrugated substrate. The first conjugated polymer DFB laser was demonstrated by McGehee et al. in 1998 [31]. Since then, DFB lasers have been demonstrated using polyfluorenes [32–39], derivatives of poly(phenylene vinylene) [23, 31, 40–43], ladder-
type poly(\textit{para}-phenylene)s [44–48], and even small molecules [45, 49–57]. DFB lasers can exhibit very low thresholds. Threshold pump pulse energies of a few nanojoules are common in one-dimensional (1D) DFB lasers, and they can even be below 200 pJ [37]. More complicated organic two-dimensional (2D) feedback lasers have been attracting much attention recently due to their low thresholds and the possibility of two-dimensionally confined output beams. Such structures can either be in form of photonic crystals [33, 48, 52, 58–60], circular DFB resonators [39, 61–66], and even random-scattering structures [67–69]. In the following subsections, the fundamentals of distributed feedback for the structures used in this work will be explained.

2.7.1 One-Dimensional DFB Resonators

To simplify the theoretical description of this approach, we consider the periodical spatial modulation to be of sinusoidal form. For a detailed discussion, please refer to [9, 28, 70]. Here, we incorporate a sinusoidal modulation of the refractive index $n$ such as

$$n(z) = \bar{n} + n_1 \cos \left( \frac{4\pi \bar{n}}{\lambda} z \right),$$  \hspace{1cm} (2.43)

and a modulation of the gain coefficient

$$g(z) = \bar{g} + g_1 \cos \left( \frac{4\pi \bar{g}}{\lambda} z \right),$$  \hspace{1cm} (2.44)

into a polymer waveguide, where $\bar{n}$ and $\bar{g}$ are the average values of the refractive index and the gain coefficient. The amplitudes of the spatial modulation are given by $n_1$ and $g_1$, while $\lambda$ is the wavelength of the Bragg scattered light. The modulation of the refractive index is determined by the respective refractive indices of the polymer gain medium and the grating substrate, as well as the desired wavelength and thus the grating period. The modulation of the gain coefficient is also determined by the grating period.
Figure 2.4: Schematics of a periodic spatial refractive index modulation in a DFB resonator of length $L$. Arrows indicate the partial reflections of a right travelling wave which add up to the left travelling wave. Feedback by first ($m = 1$) and second order ($m = 2$) Bragg scattering is indicated.

and gain coefficient of the active material. Figure 2.4 shows a simplified illustration which demonstrates the operation of a DFB resonator.

A good understanding of the feedback mechanisms in such a structure is provided by the coupled wave theory. The following considerations are according to the work of Kogelnik and Shank [70]. A spatially periodic structure such as given in equations (2.43) and (2.44) provides a strong frequency selective coupling between two counter propagating waves if the Bragg condition

$$m\lambda_{\text{Bragg}} = 2n_{\text{eff}}\Lambda$$

is fulfilled. Here, $n_{\text{eff}}$ denotes the effective refractive index of the device with grating period $\Lambda$. The characteristic wavelength $\lambda_{\text{Bragg}}$ is called the Bragg wavelength and signifies the spectral position where the coupling process between two counter propagating waves becomes exceedingly strong [7]. The integer $m$ indicates the order of the grating ($m = 1, 2, 3, ...$) which determines the emission mode of the laser. This means that in a DFB grating of order $m$, in-plane feedback is provided by the $m^{th}$ scattering order, while all lower Bragg orders couple light out of the waveguide. Figure 2.4 shows the situation for second order Bragg scattering ($m = 2$) within the plane,
and first order \((m = 1)\) Bragg scattering which emits perpendicularly to the surface. The figure indicates two waves, one that travels to the right and one that travels to the left. As each wave propagates through the structure, it continuously receives light from the counter propagating wave by Bragg scattering. This provides a form of feedback which is distributed throughout the device. To ensure that the coupling process works at its optimum, the spatial index modulation, i.e. the interfaces between the two different refractive indices, must be placed in such a way that the partial reflections of the incident waves from each successive interface add up with each other \([9]\).

The field inside the waveguide consists of two counter running waves \(A(z)\) and \(B(z)\). These waves grow in amplitude as they propagate along the \(z\) axis due to the presence of gain, and transmit energy into each other by means of Bragg scattering. The field can be written

\[
E(z) = A(z)E_0(x, y)e^{i(\omega t - \beta z)} + B(z)E_0(x, y)e^{i(\omega t + \beta z)},
\]

(2.46)

where \(\omega\) is the angular frequency and \(\beta\) is the modal propagation constant. \(E_0(x, y)\) is the wavefunction of the fundamental mode in an unperturbed medium. \(A(z)\) and \(B(z)\) are the mode amplitudes which represent the coupling between the waves. Substituting equation (2.46) into the wave equation using equation (2.33), neglecting the second derivative, limiting to the Bragg wavelength region, and adding gain term, yields \([9]\)

\[
\frac{\partial}{\partial z}A - (\bar{g} - i\delta) A = -i\kappa B
\]

\[
\frac{\partial}{\partial z}B + (\bar{g} - i\delta) B = i\kappa A
\]

(2.47)

where \(\bar{g}\) is the average gain coefficient for the mode and \(\delta \approx \beta - \beta_{\text{Bragg}}\) is the detuning factor of the wavelength against the Bragg wavelength. These two equations describe the wave propagation of two counter running coupled waves. The coupling strength is determined by the coupling coefficient \(\kappa\) which itself is influenced by the design of the laser. A more detailed discus-
The general solution to the coupled wave equations 2.47 is given by [70]

\[ A = a_1 e^{\gamma z} + a_2 e^{-\gamma z} \]
\[ B = b_1 e^{\gamma z} + b_2 e^{-\gamma z} \]

where \( \gamma \) is the complex propagation constant and can be described by

\[ \gamma^2 = \kappa^2 + (\bar{g} - i\delta)^2. \]

Depending on the choice of parameters \( \bar{g} \) and \( \kappa \), three different regimes arise for the propagation constant \( \gamma \). Accordingly, three distinct situations with significantly different properties have to be distinguished: index coupling \((\bar{g} = 0 \text{ and } \kappa \text{ real})\), gain coupling \((\bar{g} = 0 \text{ and } \kappa \text{ imaginary})\) and complex coupling \((\bar{g} > 0)\). In the case of index coupling, there is a spectral region close to the Bragg wavelength where \( \gamma \) has real values. No waves can propagate in this region which is known as photonic bandgap. Hence, laser emission does not occur at the Bragg wavelength but at wavelengths corresponding to the edges of the photonic bandgap for which propagation is just possible [70]. This is found in DFB lasers with a deep grating profile [35]. The case for DFB lasers with a shallow grating is that of complex coupling, where gain is not negligible and lasing can occur within the photonic bandgap [33, 45]).

### 2.7.2 Two-Dimensional DFB Resonators

The concepts of distributed feedback discussed so far can be extended to two-dimensional periodic modulations which consist of a superposition of two single linear gratings rotated by 90° with respect to each other. The aim of two-dimensional DFB (2D DFB) lasers is to achieve a better transverse mode confinement compared to one-dimensional DFB (1D DFB) lasers. First experiments with 2D DFB resonators in the late 1970s and early 1980s showed that the divergence of laser beams could be significantly reduced [71, 72].
the following years, there was only little research effort in this field until a theoretical investigation of photonic band structures of 2D DFB resonators was published by Bullock et al. in 1993 [73]. Since then, more and more investigations were made due to successful demonstrations of photonic crystal lasers [58, 74–76]. Figure 2.5 shows atomic force microscope (AFM) images as examples of a 1D and 2D DFB structure.

Due to much stronger photon confinement within the gain region the 2D modulation provides lasing with superior performance concerning threshold and beam quality. In contrast to 1D DFB lasers, the beam of the 2D DFB laser can be annular in profile which is caused by the two-dimensional confinement [33].

### 2.7.3 Circular Bragg Resonators

To further enhance optical confinement, a resonator geometry providing feedback from more than two directions is desirable. The optimum configuration for this is a circular resonator which in theory provides 360° in-plane feedback. The necessary feedback in one- and two-dimensional DFB resonators is provided by backscattering from the grating. In circular Bragg resonators (CBR), the feedback mechanism is essentially the same with the difference that here the propagating and counterpropagating
waves are Bessel functions in nature, and transform into each other in the centre of the grating. Figure 2.6 shows a schematic view of a typical CBR geometry. CBRs represent an interesting and very useful class of resonators that, among other attributes, can provide very low threshold operation and an ultra-small modal volume with high quality factor ($Q$), and that naturally produce a well-defined circularly symmetric output [61, 64, 65, 77–83]. The $Q$ factor is defined as the ratio of the peak laser wavelength, $\lambda_0$, to the FWHM linewidth, $\Delta \lambda$ of the resonance

$$Q = \frac{\lambda_0}{\Delta \lambda}. \quad (2.50)$$

Originally demonstrated in the field of inorganic semiconductor lasers [77–80], several polymer-based structures, operating largely in the green and red wavelength regions of the visible spectrum, have recently been reported [61, 64, 65]. CBRs support circular modes, with the electric field amplitudes for these modes determined from solutions of the Helmholtz equation in cylindrical coordinates. As with conventional linear DFB-based resonators, the interfaces between low and high refractive indices should be positioned
so that the partial reflections from each successive spatial modulation all add up in phase [77]. In the case of CBRs, the optimal grating design would then ideally employ a non-periodic modulation profile in order to closely match the nulls/maxima of the corresponding \( m^{th} \)-order Bessel function [81–83]. Lower lasing thresholds, improved mode discrimination and, in particular, a higher \( Q \) factor for the resonator might then be expected [83].

The criteria for determining the exact modulation profile of the refractive index within a circular Bragg resonator can be made in analogy to the criteria for a one-dimensional Bragg resonators as described in Chapter 2.7.1. In order to ensure that a linear dielectric modulation has a large reflection coefficient, the interfaces between low and high refractive index must be placed such that the partial reflections of an incident wave from each successive spatial modulation all add up in phase with one another. This can be achieved by placing them at the nulls or maxima of the eigenmodes, which corresponds to reflections with or without a phase jump. Hence, one needs non-periodic circular grating structures which are adjusted to the shape of the eigenmodes. A more specific description of the design procedure will be given in Chapter 6.2.
Bibliography


Chapter 3

Experimental Techniques and Materials

3.1 Introduction

This chapter discusses the general film and device preparation and characterisation techniques used within the course of this work. Individual techniques pertaining to specific work will be discussed at the beginning of the relevant chapter. Thin films of conjugated polymeric semiconductors are deposited on nanopatterned substrates by spin coating from solution. Surface profilometer and transmission spectroscopy serve for the basic characterisation of the film thickness. Photophysical measurements include the absorption and photoluminescence spectra of thin films, as well as ASE measurements. Also, the experimental setup for the characterisation of the properties of distributed feedback lasers under intense optical excitation is presented.

The organic semiconducting materials employed during the course of this work are introduced after the experimental sections. As mentioned in the Introduction, there has been an increasing interest in conjugated polymers as a new material class for optoelectronics ever since the 1990s. Also, a number of reports on lasers based on conjugated polymers that can emit across the whole visible spectrum have been published [1–14]. Especially polyfluorenes have established themselves as a particularly attractive class of gain materi-
als [4, 15–18]. As far as gain materials are concerned, polyfluorenes exhibit a number of characteristics that make them very attractive, such as strong gain, high PLQE, and high thermal and oxidative stability. It is noteworthy at this point to mark that all investigations and laser experiments have been performed in air.

### 3.2 Sample Preparation

Standard 1D-DFB gratings were fabricated by the Centre for Integrated Photonics (CIP Technologies). For experiments with multilayer devices, ITO coated quartz substrates (Spectrosil B) were used (CIP Technologies). The ITO thickness is 70 nm with a grating modulation depth of ∼50 nm. More detailed information about the characteristics of these substrates can be found in Section 5.2.

All polymer solutions were made in a cleanroom environment at room temperature. The polymers were weighed and put into new vials that had been pre-cleaned with a jet of nitrogen. Known volumes of solvents (either toluene or chlorobenzene) were added into the vials using a calibrated pipette (Eppendorf Research). All samples were pre-cleaned with acetone and then twice in isopropyl alcohol in an ultrasonic bath for durations of 15 minutes each. Afterwards, the substrate surfaces were given a plasma ashing treatment for one minute in order to remove organic and chemical residua. The respective polymer thin films were then deposited from the solutions by spin casting, which is a relatively cheap and reliable technique to produce good quality films. As displayed in Figure 3.1 the substrate is placed on the chuck and locked in place by means of vacuum. It is covered with the solution containing the dissolved polymer. Upon spinning the sample, the surplus solution is cast away with a homogeneous film remaining. The residual solvent evaporates when the sample is kept at elevated temperatures. The resulting film thickness depends on the molecular weight of the polymer, as well as the concentration of the solution, and the spin-frequency [19]. More
Figure 3.1: Schematics show the preparation of polymer thin films by spin casting from solution.

Information on the concentrations of the used solutions will be given in later in Section 3.7. For laser measurements, the polymers were spincoated onto grating substrates, whereas Spectrosil B substrates were used for all other optical characterisation experiments.

When it comes to multilayer structures, the fabrication process is limited by the demand for orthogonal solvents, which means that a polymer layer that is soluble in an unpolar solvent like toluene can only be deposited on a material that is soluble only in a polar solvent like water. Thus, in the absence of e.g. a cross-linking step, the number of layers is very limited if the spin casting technique is applied.

Thickness measurements were carried out with a Tencor Instruments alpha-step 200 surface profilometer, with a \( \sim 5 \) nm resolution. The thin film was first carefully scratched and then placed under the tip of the profilometer. The tip was then moved across the scratch, and its vertical position plotted against the horizontal position. Due to local thickness variations, this was repeated at different positions on the sample to get an average value (film thicknesses are typically \( \pm 7 \) nm from the average).
3.3 Absorption Measurements

Absorption measurements of polymer thin films were carried out at room temperature employing a dual beam Jasco UV-Vis Spectrophotometer with a spectral range of 190 to 900 nm. The schematic setup of it is shown in Figure 3.2. The light source is made up of two lamps, a deuterium lamp covering the UV regime, and a tungsten halogen lamp for the visible part of the spectrum. A flipping mirror determines which emission is channelled into the monochromator, where the beam is dispersed via two gratings. The spectrally dispersed light then passes through a narrow slit which acts like a band pass to produce monochromatic light. This monochromatic light is then split into two identical beams and guided through the reference, as well as the sample path. Both transmitted light beams are measured simultaneously by the photomultiplier tube. The ratio of both results is used to calculate the absorbance

\[
A = \log_{10} \left( \frac{T_{\text{ref}}}{T_{\text{sample}}} \right),
\]

(3.1)

where \( T_{\text{sample}} \) is the light transmission through the measured sample and \( T_{\text{ref}} \) is the light transmission through the reference substrate. The detection limit of this machine is an \( A \) of 3. However, results over 2.5 already show significant noise.

The thickness-independent and hence more meaningful value absorption coefficient \( \alpha \) can be calculated for single layers with film thicknesses \( d < \lambda/2 \) by using the Beer-Lambert law

\[
\alpha = \frac{A \ln(10)}{d}.
\]

(3.2)

For multilayer waveguides, the results of this measurement may be distorted due to internal reflections (Fabry-Perot effect). In this case, equation 3.2 can only be considered as an approximation.
3.4 Photoluminescence Measurements

To study the vibronic and optical properties of a conjugated polymer (c.f. Section 1.3), photoluminescence spectroscopy proves to be a very powerful tool. Photoluminescence measurements were obtained on the same samples by a Horiba FluoroMax 3 spectrofluorometer at room temperature. The excitation light is provided by steady-state monochromated light from a 150 W xenon arc lamp, and its wavelength- and time-dependent intensity is measured by a photodetector. The photoluminescence from the gain polymer is collected via another monochromator and a photomultiplier tube. This technology provides an extremely high signal-to-noise ratio of 2500:1 [20]. The system was calibrated with correction files for all excitation and emission wavelengths. During the course of this work, the excitation wavelength for recording PL spectra was fixed at 355 nm, which is the emission wavelength of the excitation laser (c.f. Section 3.5 and 3.6). Likewise, quantitative measurements of the PL quantum efficiency (PLQE) were obtained using this spectrofluorometer together with an integrating sphere attachment [21]. PLQE is the ratio of the number of photons emitted to the number of pho-
tons absorbed by a material or a sequence of materials. Finally, time-resolved fluorescence was performed by time correlated single photon counting (TC-SPC) using a HORIBA Jobin Yvon IBH Fluorocube.

3.5 Amplified Spontaneous Emission Measurements

The polymer films were photopumped using a frequency-tripled Nd:YAG laser, working at 355 nm, delivering ∼23 ns pulses at a repetition rate of 10 Hz. A schematic layout of the setup used for the ASE measurements is shown in Figure 3.3. The pulse energy incident on the sample was adjusted by the insertion of calibrated neutral density filters (ND) into the beam path. The pump laser beam was focused with a cylindrical lens and spatially modified with an adjustable slit to form a narrow excitation stripe on the polymer surface of dimension 200 µm × 4 mm. The emission of the LEP was recorded by an optical fibre placed at the edge of the sample, wavelength dispersed by a spectrometer (Princeton Instruments Acton SpectraPro 2300i) and detected with a charge-coupled device (CCD) (Princeton Instruments Pixis400).

One experimental challenge in an ASE measurement is to reduce the noise by PL emission from the sample. In order to explain this issue, Figure 3.4 illustrates the typical ASE characteristics of investigated devices. The left part indicates three input energy dependent regimes. In order to understand this behaviour, we have to take into account both emission processes that take place in the LEP film: PL and ASE. Whereas PL is undirected and unpolarised, ASE is highly directional and linearly polarised [22, 23].

Regime (a) signifies the input fluence range in which the detected PL outweighs the waveguided ASE. As the input fluence is increased, waveguided spontaneous emission experiences stronger amplification and eventually dominates the edge emission. This process can be easily understood by applying
the rate equation that describes the photon density (c.f. Section 2.3). Equation 2.13 includes one term to characterise PL ($\beta N_2/\tau_R$) and one for ASE ($B_{21}S(N_2 - N_1)$) which states a proportional dependence on the photon density and hence the input fluence. This relation leads to the slope change in regime (b). Regime (c) then signifies gain saturation. The right part of Figure 3.4 illustrates both processes independently. In order to optimise the experimental setup, the detection of PL has to be reduced to a minimum. This would basically mean to offset the PL curve to lower values and hence reduce the detected onset of ASE. By using an iris (diameter of 60 $\mu$m), a polariser and a near-UV transparent microscope objective (Mitutoyo Plan NUV, NA = 0.4) that focuses on the sample edge, this could be achieved to a certain degree.

To determine the absorbed pulse energy $E_p$ on the sample, an energy meter (Ophir Nova II) with a pyroelectric head was used. It was measured at the position of the sample before and after the measurement run.
Figure 3.4: Left figure shows typical ASE output as a function of input energy density. Regime (a) is light from spontaneous emission, (b) change of slope indicates ASE, and flat slope in (c) is due to gain saturation. The right figure depicts both ongoing natures of emission. $\Delta E$ indicates the error in determining the threshold of ASE due to PL noise.

Figure 3.5: Experimental setup for the spectral characterisation of lasers.

3.6 Laser Measurements

A schematic of the employed experimental setup is shown in Figure 3.5. The investigated polymer laser devices were optically excited with $\sim 23$ ns pulses from a frequency-tripled, Q-switched Nd:YAG laser, emitting at $\lambda = 355$ nm with a repetition rate of 10 Hz.

The pulse energy incident on the sample was adjusted by the insertion of calibrated ND filters into the beam path. An iris was used to improve the
beam quality by cutting out artifacts in the profile of the transverse mode. Afterwards, a telescopic arrangement was used to adjust the beam diameter such that it filled out the entrance of a near-UV transparent microscope objective (Mitutoyo Plan NUV). As shown in Figure 3.5, two pellicle beamsplitters were inserted into the beam path to produce an optical monitoring system through which the excitation spot could conveniently be localised on the sample. The right beamsplitter reflected light from a halogen light source into the microscope objective and hence illuminated the sample surface. The left beamsplitter guided the reflection from the sample into a CCD camera which was connected via USB with a PC.

The emission from the samples was recorded using the same optical fibre-coupled spectrometer and CCD as for the ASE measurements. Since both transparent and opaque substrates were employed during the course of this work, different arrangements for the signal detected had to be used. Therefore, each following chapter contains a brief section on specific experimental details.

### 3.7 Polymer Gain Materials

One approach to lowering the laser thresholds has been to shift the emission to longer wavelengths in order to reduce ground state absorption. However, results from Stevens et al. have shown that this is disadvantageous for two reasons [24]:

1. The presence of excited-state absorption at longer wavelengths (e.g. from charges and excitons) can introduce significant losses.

2. The rate of exciton quenching through the Förster mechanism (due to the overlap of PL and exciton absorption) is increased by redshifting the laser wavelength.
Their findings suggest that gain materials emitting in the violet or blue part of the spectrum will be the most suitable for laser applications since these exhibit the lowest losses due to excited-state absorption and Förster annihilation. In the following, this chapter presents a study of the properties of a variety of different blue emitting polyfluorenes that exhibit optical gain and hence are attractive for laser applications: the copolymer FOP, the statistical copolymer BN-PFO, and the statistical copolymer Y80F8:20F5.

3.7.1 FOP

The copolymer poly(9,9-dioctylfluorene-co-(2,5-dioctyloxy)-p-phenylene) (FOP) shown in Figure 3.6 emits in the violet and blue spectral region. The material studied in this work was synthesized at The Dow Chemical Company. Slab waveguides and laser devices were fabricated by spin coating thin-films from 16 mg/ml tetrahydrofuran (THF) solutions. The solvent THF was used because in the case of FOP it was found to give the best film quality compared with other investigated solvents such as toluene and chloroform. The substrate was then spinned for 40 s at rotation speeds between 2500 - 2700 rpm, to give film thicknesses between 120 and 150 nm.

Figure 3.7 shows the absorption coefficient $\alpha$, PL and ASE spectra of FOP slab waveguides on Spectrosil B substrates. The absorption spectrum has a peak at 372 nm and a shoulder at 308 nm, with corresponding absorption coefficients of $1.6\times10^5$ and $4.5\times10^4$ cm$^{-1}$. The PL spectrum is relatively structureless, with two poorly resolved peaks located at 417 nm (0-0 transition) and 435 nm (0-1), and a shoulder near 478 nm (0-2). Absorption and
Figure 3.7: Absorption coefficient (left coordinate), PL (dashed), and ASE (filled area) spectra of FOP slab waveguides.

PL spectra exhibit only a small overlap which is important for waveguiding as it reduces the effects of re-absorption in the film [25, 26]. From the intersection of the absorption and PL spectra a band gap energy of 3.1 eV can be estimated\(^1\). The chemical structure of FOP is very similar to the prototypical example of polyfluorenes, PFO [15]. However, the dioctyloxy side chains in FOP twist the backbone and hence shorten the conjugation length [27, 28]. As a consequence, its spectral features resemble those of PFO but are generally blue-shifted: the absorption peak by \(\sim 10\) nm and the PL peak (0-0) by \(\sim 22\) nm. The peak absorption coefficient of both materials is approximately the same. As Figure 3.7 shows, the maximum net gain occurs at \(\lambda_{\text{ASE}} = 435\) nm, which coincides with the 0-1 transition of the FOP spontaneous emission spectrum. The PLQE measured using the integrating sphere is 35 \(\pm\) 5%.

\(^1\)The energetic difference between HOMO and LUMO shall be considered as band gap energy.
3.7.2 BN-PFO

A promising blue emitting material is the copolymer consisting of 2,7-(9,9-dioctyfluorene) repeat units with a minor portion of statistically incorporated 6,6-(2,2-octyloxy-1,1-binaphthyl) spacer groups (BN-PFO). In the case of this thesis, the amount of binaphthyl spacer groups was 12.7%. The chemical structure of BN-PFO is shown in Figure 3.8 [10]. Rabe et al. have shown that the incorporation of these spacer groups into the PFO backbone hinders the formation of the highly ordered \( \beta \)-phase chain formation [10], which could otherwise occur in thin-films of the homopolymer and alter both absorption and emission spectra [29–31]. The significant effect of the \( \beta \)-phase on the refractive index was shown as well [32]. With an increasing spacer concentration in the backbone, the laser thresholds could be reduced steadily [10], and have been among the lowest thresholds report thus far [12]. The BN-PFO was synthesised at the group of Professor Scherf at Bergische Universität Wuppertal, Germany. Slab waveguides and laser devices were fabricated by spin coating thin-films from 16.4 mg/ml toluene solutions. The substrate was then spun for 40 s at rotation speeds between 4600 - 6500 rpm, to give film thicknesses between 80 and 160 nm.

Figure 3.9 shows the absorption coefficient \( \alpha \), PL and ASE spectra of BN-PFO slab waveguides on Spectrosil B substrates. The featureless absorption spectrum is broader than FOP and peaks at 374 nm. The absorption coefficient at this wavelength is \( 3.1 \times 10^5 \) cm\(^{-1} \). The PL spectrum shows a structures emission that exhibits two vibronic peaks at 421 nm (0-0 transition),
445 nm (0-1), and a shoulder around 480 nm (0-2). As in the case of FOP, the absorption and emission spectra only show a small overlap. From their intersection a band gap energy of 3.0 eV can be estimated. The measured PLQE is 48 ± 5%.

### 3.7.3 Y80F8:20F5

Another very promising polyfluorene is a statistical copolymer which is made up of 80% 9,9-dioctylfluorene and 20% 9,9-di(2-methyl)butyl side chains (Y80F8:20F5), Figure 3.10 shows its chemical structure. The polymer synthesis was carried out at the Sumitomo Chemical Company, Ltd. Tsukuba Research Laboratory, Japan, and extensively studied by Dr Boon Kar Yap [33]. Slab waveguides and laser devices were fabricated by spin coating thin-films from 10 mg/ml toluene solutions. The covered substrate was then spun for 40 s at rotation speeds between 2000 - 4000 rpm, to give film thicknesses between 80 and 130 nm.

Figure 3.11 shows the absorption coefficient $\alpha$, PL and ASE spectra of Y80F8:20F5 slab waveguides on Spectrosil B substrates. The absorption spectrum has a minor peak near 296 nm, and a main peak at 383 nm,
with corresponding absorption coefficients of $2.8 \times 10^4$ and $2.5 \times 10^5$ cm$^{-1}$. The PL spectrum has two distinct vibronic peaks at 426 nm (0-0 transition) and 450 nm (0-1 transition), and two clear shoulders around 473 nm (0-2 transition) and 515 nm (0-3 transition). As in both other cases as well, the absorption and PL spectra exhibit only a small overlap. From their intersection a band gap energy of 3.0 eV can be estimated. The ASE spectrum has its maximum at 450 nm. In this work, measured PLQE is $68 \pm 5\%$ which is among the highest values reported so far for conjugated polymers [34]. Previous measurements have also found that Y80F8:20F5 has a net gain of 87 cm$^{-1}$ at $\lambda = 448$ nm and an excitation energy of 3 $\mu$J [34].

Table 3.1 summarises the optical properties of the three studied polymers.
Table 3.1: Photophysical properties of FOP, BN-PFO and Y80F8:20F5.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Gain maxima (nm)</th>
<th>Absorption coefficients ($\times 10^5$ cm$^{-1}$)</th>
<th>PL maxima (nm)</th>
<th>ASE wavelength (nm)</th>
<th>PLQE (% ± 5%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FOP</td>
<td>308, 372</td>
<td>0.48, 2.2</td>
<td>417, 435, 478</td>
<td>435</td>
<td>35</td>
</tr>
<tr>
<td>BN-PFO</td>
<td>374</td>
<td>3.1</td>
<td>421, 445, 480</td>
<td>447</td>
<td>48</td>
</tr>
<tr>
<td>Y80F8:20F5</td>
<td>296, 383</td>
<td>0.28, 2.5</td>
<td>426, 450, 473, 515</td>
<td>450</td>
<td>65</td>
</tr>
</tbody>
</table>

3.8 Refractive Indices

Variable-angle spectroscopic ellipsometry (VASE) was carried out by Dr Mariano Campoy-Quiles and Toby Ferenczi on thin films of BN-PFO and Y80F8:20F5 prepared on Spectrosil B substrates. The corresponding complex optical constants ($\bar{n}(\lambda) = n(\lambda) + i\kappa(\lambda)$) data was derived from the ellipsometric angles. More detailed information about this measurement procedure including the exciton model can be found elsewhere [35, 36]. Both Kramers-Kronig relation and the accepted results from PFO (e.g. [32]) were employed by Dr Paul Stavrinou to obtain the refractive index, $n$ of FOP from the measured absorption coefficient, $\alpha$. The extinction coefficient, $\kappa$, relates to the absorption coefficient via

$$\kappa = \frac{\alpha \lambda}{4\pi}. \quad (3.3)$$

However, it has to be noted that $n$ and $\kappa$ values yielded from ellipsometry measurements are not consistent with those deduced from Kramers-Kronig relations. As both the refractive index as well as the extinction coefficient vary with film morphology, one should act with caution when comparing ellipsometry results for a material with the literature.

Figure 3.12 shows the refractive indices, $n(\lambda)$, deduced for FOP, BN-PFO and Y80F8:20F5. According to these results, the refractive index of FOP is $\sim$1.72 at the ASE wavelength of $\lambda_{ASE} = 435$ nm, which is slightly lower than glassy-phase PFO at its ASE wavelength. The respective refractive indices of the other polymers are 1.95 at $\lambda_{ASE} = 447$ nm in the case of BN-PFO, and 1.96 at $\lambda_{ASE} = 450$ nm in the case of Y80F8:20F5. Both
values are relatively high for conjugated polymers [36], and thus offer an advantage in terms of waveguiding, where a high refractive index of the gain material directly translates into a high modal confinement and hence high modal gain and lower losses outside the gain material. This topic will be discussed in more detail in Chapter 5, where the importance of the gain material refractive index in multilayer structures is shown. In Figure 3.13 the associated extinction coefficients of the three polymers are plotted.
Figure 3.13: Wavelength dependent extinction coefficient, $\kappa$, of Y80F8:20F5 (orange), BN-PFO (red), and FOP (blue).

### 3.9 Summary

This chapter presented the techniques and materials used during the course of this work. For this, the optical characteristics of three polyfluorenes, poly(9,9-dioctyfluorene-co-(2,5-dioctyloxy)-p-phenylene) (FOP), a copolymer consisting of 2,7-(9,9-dioctyfluorene) repeat units with a minor portion of statistically incorporated 6,6-(2,2-octyloxy-1,1-binaphthyl) spacer groups (BN-PFO), and the statistical copolymer Y80F8:20F5 which is made up of 80% 9,9-dioctyfluorene and 20% 9,9-di(2-methyl)butyl side chains, were studied. All demonstrated polyfluorenes exhibited similar spectral features, consistent with their common backbone structure. The emission of FOP is, however, some 15 nm blue-shifted with respect to BN-PFO and Y80F8:20F5, and has less pronounced vibronic peaks.
Bibliography


dioctylfluorene) and poly (9, 9-dioctylfluorene-co-benzothiadiazole),”  


[32] P.N. Stavrinou, G. Ryu, M. Campoy-Quiles, and D.D.C. Bradley, “The change in refractive index of poly(9,9-dioctylfluorene) due to the adop-


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Chapter 4

Violet-Emitting Polymer Lasers

4.1 Introduction

Over recent years, there has been strong interest in the field of lasers based on semiconducting conjugated polymers that can emit across the whole visible spectrum [1–14]. Fluorene copolymers have established themselves as a particularly attractive material class amongst organic semiconductors. Within all demonstrated polymer lasers, the emission wavelength spanned from 435 [10] to 702 nm [7], covering a wide range of the visible spectrum\(^1\). Beyond these boundaries, lasing in small molecule films has been shown at 392 nm [16], and in the ultraviolet (UV) employing spiro-linked molecules. These spiro materials have to be deposited by vacuum evaporation [17], or can be processed from a chloroform solution [18]. This chapter reports on thin-film DFB lasers based on the copolymer poly(9,9-dioctylfluorene-co-(2,5-dioctyloxy)-p-phenylene) (FOP), operating in the violet, between 418.9 and 447.1 nm and hence partly within an emission window that has not yet been covered by organic lasers. The optical characterisation of FOP is given in Sections 3.7.1 and 3.8.

\(^1\)A typical human eye will respond to wavelengths from 390 to 780 nm [15].
Figure 4.1: SEM image of a SiO$_2$ DFB grating taken at normal incidence. Brighter regions are the top and the side surfaces of the corrugation, dark regions are the trenches.

Figure 4.2: Schematic cross section through a laser structure.

4.2 Experimental Details

The lasers are made under clean room conditions by spin coating thin polymer layers on top of DFB grating substrates based on SiO$_2$, to produce asymmetric slab waveguides that support only the fundamental transverse electric (TE$_0$) and transverse magnetic (TM$_0$) modes for the wavelengths of interest. A scanning electron microscopy (SEM) image of such a DFB grating is shown in Figure 4.1.

Figure 4.2 shows the square-shaped grating structure of such a DFB resonator. The duty cycle of a DFB is given by the ratio between groove
width, $w$, and grating period, $\Lambda$,

$$dc = \frac{w}{\Lambda} \quad (4.1)$$

The gratings have periods of $\Lambda \approx 270$ nm and 290 nm, and duty cycles of $dc \approx 36\%$ and 28\% respectively. The modulation depth, $d_g$ of the gratings is 70 nm. Thin polymer films are deposited on top of the gratings from 16 mg/ml THF solutions, to form the gain polymer layer for each laser sample. By varying the spin speed, FOP film thicknesses between 95 and 140 nm can be realised. To investigate the lasing performance of the FOP devices, the samples are optically-pumped at 355 nm with a circular pump spot (diameter 100 $\mu$m) from a frequency-tripled, Q-switched Nd:YAG laser as described in Section 3.6.

### 4.3 Violet Polyfluorene Lasers

Figure 4.3 (a) shows the emission spectra of one of the FOP lasers for excitation intensities below and above threshold. For pump fluences below the lasing threshold, the emission spectrum consists of of the normal broad, low intensity PL spectrum which is strongly modified by Bragg scattering due to the presence of the grating. In particular, the spectrum is dominated by two peaks which are due to waveguided PL that is Bragg scattered out of the waveguide at an angle normal to the surface. The spectrum also exhibits a characteristic dip which corresponds to the photonic stop band in which wave propagation is inhibited [19–22]. For higher pump intensities laser oscillation occurs in close proximity to the Bragg wavelength $\lambda_{\text{Bragg}} = \Lambda n_{\text{eff}}$ and a sharp laser line starts dominating the spectrum. This illustrates very clearly the effect of complex coupling (including a contribution of gain coupling) on the laser wavelength. This FOP laser operates at 422.6 nm and has a FWHM of 0.8 nm. The laser input-output characteristic is presented in Figure 4.3 (b) which shows the dependence of the peak emission on the
pump fluence. A laser threshold can clearly be observed by a sudden change in slope followed by a linear increase of the output emission as the pump intensity is further increased. The threshold fluence is 26.6 $\mu$J/cm$^2$.

Figure 4.3: (a) Normalised emission spectra of a FOP DFB laser, taken below (blue) and above (red) the lasing threshold. (b) Peak output signal from the same laser as a function of the pump fluence per pulse.

For the investigation of FOP as a gain material for laser applications, a range of DFB devices are fabricated on two sets of gratings, with $\Lambda = 270$ nm and 290 nm. The film thicknesses varied between 95 nm and 200 nm. Figure 4.4 shows a corresponding selection of laser peaks together with the PL spectrum of FOP with vibronic structures around 417 nm and 435 nm. The PL spectrum is measured for a film on an unpatterned substrate using a spectrofluorimeter. When the sample is excited on the grating, laser emission can be observed. In a second order one-dimensional DFB grating, this is indicated by a characteristic fan-shaped far field emission pattern. Above laser threshold the emission pattern changes from being homogenous radiation into the forward spatial hemisphere, to an anisotropic beam with large divergence in the direction parallel to the grating trenches, and very low divergence orthogonal to them [23]. The shortest wavelength emission at 418.9 nm comes from a TM mode, readily identified by its polarisation (c.f. Figure 2.2). The longest measured laser wavelength is 447.1 nm and from a TE mode. Beyond these wavelengths, no laser emission can be observed although the grating periods would also be suitable for those spectral re-
gions. This fact indicates that the optical gain below 418.9 nm and above 447.1 nm in these devices is not high enough to compensate for the modal losses and drive the laser beyond threshold. The observed laser peaks exhibit linewidths between 0.44 nm and 2.11 nm, in which the latter is measured with a lower spectral resolution and is therefore resolution limited. All other laser peaks were much broader than the resolution limit permitted. The laser spectrum of a DFB laser with grating period $\Lambda = 270$ nm is shown more clearly in Figure 4.4 (b).

Figure 4.4: (a) PL spectrum of FOP (dashed) and emission spectra of the FOP DFB lasers with grating periods/film thicknesses: A: 270 nm/110 nm, B: 270 nm/105 nm, C: 270 nm/135 nm, D: 270 nm/200 nm, E: 290 nm/95 nm, F: 290 nm/115 nm, G: 290 nm/140 nm. Note that laser peak A represents a TM mode whilst the others are all TE modes. Peak G is collected with a lower spectral resolution. (b) Expanded spectrum for a 430.9 nm laser (data points). Gaussian fit (solid line) and FWHM are also shown.

From these wavelength tuning results effective refractive indices between 1.514 and 1.596 can be deduced using the Bragg condition for second order gratings according to equation (2.45). For both grating periods it increases virtually in a linear fashion: from 1.566 at 422.7 nm to 1.596 at 430.9 nm for the 270 nm grating, and from 1.514 at 439.1 nm to 1.538 at 446 nm for the 290 nm grating.

In addition to the spectral characteristics, the input-output characteristics of the individual laser samples are investigated. The threshold fluences extracted from these measurements are plotted in Figure 4.5 (b) versus the
respective laser wavelength. The lowest laser threshold of 9 \( \mu \text{J/cm}^2 \) is obtained close to the ASE wavelength at 435 nm for a grating period of 270 nm with a film thickness of 200 nm. Towards shorter wavelengths increasing self-absorption and towards longer wavelengths decreasing material gain cause a significant increase in threshold and lead to threshold maxima for the studied spectral range of 26.7 \( \mu \text{J/cm}^2 \) at 422.7 nm, and 102 \( \mu \text{J/cm}^2 \) at 446 nm. Considering a pump pulse length of 23 ns, the minimum power density to reach the laser threshold becomes 391 W/cm\(^2\) for the 430.9 nm laser.

![Figure 4.5](image.png)

Figure 4.5: (a) Effective refractive indices of the DFB TE laser modes for (blue) \( \Lambda = 270 \text{ nm} \) and (red) \( \Lambda = 290 \text{ nm} \) grating samples. (b) Laser threshold fluences. The dashed curve serves as a guide to the eye.

As mentioned above, in some cases, in addition to the TE mode, a weak signal from a TM polarised laser mode can be detected. While TE modes are characterised by an electrical field vector parallel to the grating trenches, TM modes have magnetic field vectors perpendicular to the trenches. Both modes can operate simultaneously, while the TM mode is always blue-shifted due to the weaker optical confinement of TM waves inside the organic film and hence the lower effective refractive index. A polarisation filter is used to distinguish between TE and TM modes. Figure 4.6 shows the emission spectra through the polarisation filter. The emission at \( \lambda = 440.5 \text{ nm} \) is almost wholly composed of TE polarised radiation. The residual TM polarised emission is 1/50 that of the TE emission.

An interesting behaviour is revealed when plotting the laser wavelength ver-
Figure 4.6: Polarisation characteristics of laser emission spectra. The emission is composed of TE and TM modes, with the output signal at $\lambda = 440.5$ nm dominated by TE polarised emission. The TM polarised emission is only $\sim 1/50$ of the TE polarised emission.

The measurements of these FOP DFB lasers disclosed the problem that the number of oscillating modes and hence the FWHM of the laser emission...
depends highly on the size of the pump spot. Figure 4.8 shows the recorded spectra for two measurements taken on the same sample location with different excitation area spot diameters. Due to slight variations in the film thickness and the quality of the DFB, both effective refractive index and grating period may change across the active region. As long as the active region is limited to several dozen microns, single mode operation can be observed. However, if this area becomes too large, a pronounced multi mode operation will result, as shown in the right part of Figure 4.8. In order to avoid such multi mode oscillation, the pump spot has to be focused to a suitable size.

The far-field transverse modes of the output beams from lasers with different pump spot sizes are measured by directly imaging the beams with a Gentec WinCamD beam profiler using no additional optics. The recorded output beams for diameters of 100 μm and 400 μm are shown in Figure 4.9. In the case of 100 μm pump spot, the emission pattern is fan-shaped, as expected for 1D second order DFB gratings that provide feedback only in one direction [19, 23, 26]. While the emission perpendicular to the grating trenches is strongly confined, that parallel to the trenches exhibits a high
Figure 4.8: Emission spectra of an FOP DFB laser. (a) shows single mode lasing for \( \sim 50 \) \( \mu \)m pump radius; (b) shows multi mode laser emission (indicated by three peaks) from the same sample for a \( \sim 465 \) \( \mu \)m radius. Both spectra were obtained for the same pump fluence (\( \sim 22 \) \( \mu \)J/cm\(^2\)).

divergence. Note that the colours in these images indicate the detected field intensity. The left figure shows virtually a single emission stripe with slightly frayed boundaries. However, in the centre a double-lobed pattern can be observed which has been reported in recent years [8, 27]. An explanation for this phenomenon could be that light outcoupling is weakest in the centre of the DFB resonator, where the counter-propagating waves have equal amplitudes [28, 29]. On the other hand, the modal fields at the edges of the resonator are more efficiently outcoupled and emitted as laser radiation. The combination of both processes then leads to the observed double-lobed emission profile. This proposal could explain the more pronounced double-lobe (or even treble-lobe) nature of the emitted beam in the case of a larger pump beam diameter as shown in the right part of Figure 4.9.

To what extent coupled-mode theory can be applied to describe polymer DFB lasers is not entirely clear. Limitations are set by the fact that while coupled-mode theory operates with a limited DFB resonator length and reflective end faces, polymer DFB resonators are usually much larger than the active region and have no reflective edges. The mentioned difference
Figure 4.9: (Left) Beam profiler image of a second order FOP DFB laser excited with a small pump spot (100 µm diameter). The DFB laser emission is emitted in a fan-shaped beam perpendicular to the grating structure on the substrate. The central part of the emission with higher intensities (indicated by the green and yellow colouring) features a double-lobe pattern. (Right) Same laser sample pumped by a large spot (400 µm diameter).

derives from the respective fabrication processes. Inorganic semiconductor lasers are usually cleaved at the edges of the DFB grating and these cleaved end-faces act as mirrors. In the case of polymer DFB lasers however, the grating is usually several hundreds of microns away from the substrate edges. Furthermore, due to the spin coating process from solution the 'edges' of the gain material have no clear-cut end face but rather look like a blob.
4.4 Summary

This chapter reported the characteristics of violet light emitting polyfluorene distributed feedback lasers featuring one-dimensional optical confinement. The lasers were based on the copolymer FOP and were optically-pumped by a frequency-triplet Nd:YAG laser.

Emission wavelength tuning was realised by altering both grating period and gain polymer thickness, providing lasers to cover a part of the spectral region between the blue and ultra-violet that has not been addressed yet by organic semiconductor lasing. The FOP lasers operated between 418.9 nm and 447.1 nm. The emission and operating characteristics of the laser devices were described in detail. The influence of the pump spot size on the emission characteristics was shown by spectral determination of multi mode lasing, and comparing the transverse mode profile of the output beams for small and large pump spots.

It was shown that lasers based on a shorter period grating show a weaker sensitivity to changes of the gain polymer thickness. This might prove to be a beneficial feature for sensoring applications employing polymer lasers.
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Chapter 5

Multi-Layer Structures on Conducting Distributed Feedback Resonators

5.1 Introduction

Conjugated polymers have emerged as a promising solid-state gain material class that offer access to the full visible spectrum and the prospect of compact diode lasers [1, 2]. Fluorene-based conjugated polymers in particular have proven to be attractive members of this material class, exhibiting high optical gain (\( \sim 50 \text{ cm}^{-1} \)), low losses (\( \sim 5 \text{ cm}^{-1} \)) and in some cases high charge carrier mobilities [3–9]. It has been shown in the previous chapter that optically pumped conjugated polymer lasers can be tuned even across the violet and blue spectrum. To this date, only optically pumped lasing has been convincingly demonstrated. The development of electrically pumped organic semiconductor lasers has turned out to be rather more difficult than originally hoped, due to difficulties with charge carrier injection, carrier transport and polaron-induced absorption [1, 10, 11]. The inorganic diode laser is one of the most important devices in modern optoelectronic technology and at the same time the laser diode is the last remaining device...
that has yet to be demonstrated with organic materials. Hence there is considerable interest to achieve electrically pumped organic laser action, even if this entails substantial additional research and development.

In order to address the challenges towards this goal (c.f. Section 1.1), optimised gain materials and device structures have to be developed. Having a look at established OLED architectures reveals that most of them use ITO as electrode material. Therefore, electrical injection in polymer laser diodes will likely take the same or a similar form. A generic schematic of an OLED is given in Figure 5.1.

The problem now with ITO, and in this sense with all other electrode materials, is its combination of high refractive index with high optical losses. These optical characteristics still present a major problem to potential polymer laser diodes, and one possible way to solve this is to employ a multilayer approach similar to those of OLEDs.

This chapter will therefore present a detailed study of the influence of refractive indices in a multilayer device architecture including an ITO layer. Numerical simulations and the experimental results of a thin-film single mode
blue-light-emitting conjugated polymer laser in a multilayer waveguide structure based on an ITO processed DFB resonator prove that in order to use ITO within a polymer laser device, the refractive indices of LEP and additional interlayers are crucial. By identifying the appropriate parameters and designing the device accordingly, the optical losses due to absorption in the ITO electrode can be reduced. This reduces the threshold fluence required for laser action which directly translates into a reduction in the current density required under electrical excitation.

Reufer et al. [12] have shown that a 300 nm thick organic interlayer shifts the waveguided mode sufficiently enough away from a lossy ITO contact to restore ASE and reduce its threshold drastically. However, the overall thickness of the organic layers of that device lay around 0.5 µm which is unrealistically thick for charge carrier transport. Recently, promising results in imprinting technology have shown polymer lasers on conductive substrates. Namdas et al. [13] have demonstrated optically pumped lasers based on a light-emitting field-effect transistor architecture with a DFB resonator imprinted into the light-emitting polymer (LEP). Optically pumped lasing action on one-dimensional DFB devices on ITO substrates could be achieved for pump energies above 100 nJ/pulse.

5.2 Experimental Details

A requirement for optimising the device design is a fundamental understanding of the optical environment of a waveguide influencing the performance of a laser structure. Therefore, a simulation tool for numerical mode modelling was developed. The model for the mode simulations comprises the optical properties of multilayer polymer laser structures in terms of refractive indices, layer thicknesses, layer numbers, absorption coefficients of the
Figure 5.2: Schematic structure of a four layer device comprising an ITO electrode, a homogenised grating, an inter layer and gain medium layer with constant refractive indices $n_l$, $l = 0, \ldots, 5$.

respective layers and wavelength of the propagating mode. The schematics of such a structure are shown in Figure 5.2, comprising four inner layers. For reasons of simplification, the intrinsic anisotropies of polymer films have not been taken into account [14], and the mode calculations in each layer are restricted to isotropic refractive index profiles instead.

In Chapter 2.5, the solution for plane waves in slab waveguides, equation (2.33), was derived from Maxwell’s equations. To calculate waveguide modes in a multilayer slab waveguide, equation (2.33) has to be solved with respect to following boundary conditions:

1. The solutions of $E$ have to be continuous across the boundaries of each layer.

2. The field has to decay both in the substrate and in air.

The calculated field $E_y(x)$ can then be used to determine the modal intensity profile $|E_y(x)|^2$, such as the one shown in Figure 5.3 which depicts a calculated TE$_0$ profile in a four layer waveguide structure. One important
Figure 5.3: TE$_0$ modal intensity profile, $E_y^2$, in the optical environment of a four layer waveguide device with an ITO electrode.

characteristic of such a device is the optical confinement factor $\Gamma_l$. It measures the ratio between the represented intensity in a given layer, that is from $d_l$ to $d_{l+1}$, over the total intensity of the mode.

$$\Gamma_l = \frac{\int_{d_l}^{d_{l+1}} I(x)dx}{\int_{-\infty}^{\infty} I(x)dx}$$ (5.1)

Another important factor is the waveguide loss due to absorption, $\alpha_{wg}$, which is given by the sum of the respective absorption coefficients, $\alpha_l$, of the individual layers.

$$\alpha_{wg} = \sum_{l=0}^{m} \Gamma_l \alpha_l \frac{n_l}{n_{eff}}.$$ (5.2)

The ratio between refractive index $n_l$ and effective refractive index $n_{eff}$ is analogous to the expression of modal gain [15], weighting the longer zig-zag pathlength of the propagating mode in the material.

Based on the simulation results, design considerations can be deduced and used to fabricate optimised devices. For experiments, the same laser setup as described in Chapter 3.6 was employed, and all measurements of these multilayer devices were also performed in atmosphere. Laser samples were
optically pumped from the polymer side to avoid absorption in the ITO.

5.3 Design Considerations for the Incorporation of Electrodes

As in most cases in technology, device development is not a simple one-dimensional optimisation process but rather multi-dimensional with a complex interdependence of parameters. Thus, a certain degree of trading-off will not be avoidable. One of these trade-offs with reference to the emission wavelength was already mentioned in Section 3.7. In this section, design rules addressing the optical environment of the laser device will be presented and discussed without taking non-related loss processes (e.g. excited state absorption) or electron transport into account. The simulation parameters can be found in Appendix 8.2.

5.3.1 Thickness of Inter Layer

The most simple parameter to alter is the thickness of the interlayer. Reufer et al. have demonstrated that the mode penetration into lossy electrodes (in their case ITO) can be minimised and ASE be restored by inserting a thick (300 nm) hole transport layer (HTL) between the electrode and the gain polymer [12]. With a constant thickness of the emission layer (240 nm), they have systematically increased the HTL thickness and observed a gradual reduction of the ASE threshold up to that point where the ASE threshold in absence of ITO was reinstated. However, the question arises if such thick films are suitable for polymer lasers based on a DFB architecture with a conducting grating. Connected to that is the fact that by increasing the overall thickness, one also runs the risk of having a device that supports
several modes.

The left part of Figure 5.4 shows the calculated waveguide loss due to absorption, $\alpha_{\text{wg}}$, as a function of the inter layer thickness, $d_{\text{il}}$, for a structure as depicted in Figure 5.3. The thickness of the gain polymer was kept constant at 180 nm, with a refractive index of 1.96. With no interlayer, at least a fifth of the mode is guided in the ITO layer. For very thin layers, still a large proportion of it is confined in the ITO, leading to significant losses due to absorption that explains the high pump energies needed to achieve ASE in past reports of organic light-emitting semiconductors [12, 16, 17]. For increasing thicknesses the modal shape becomes narrower and moves away from the ITO, which leads to an increase in the confinement factor in the gain polymer layer, as well as a reduction of the modal overlap with the lossy electrode. Figure 5.5 compares two extreme cases to illustrate this issue. The decrease of the waveguide loss is therefore due to the reduced overlap of the waveguided mode with the lossy ITO. By doing so, waveguide losses of $\sim 4$ cm$^{-1}$ for an overall thickness of inter layer and gain polymer of 420 nm can be obtained.

However, if an optimised laser structure is to be designed, another important factor needs to be considered as well. This factor is the coupling coefficient which describes the degree to which counter-propagating waves transfer energy into each other. It can be calculated for any geometrical form of grating [18]. The general solution is given by

$$
\kappa = \frac{\pi}{n_{\text{eff}} N^2 \lambda_{\text{Bragg}}} \int \Delta \left[ n^2(x, z) \right] |E_y(x)|^2 dx,
$$

(5.3)

where $N^2$ is a normalisation constant given by the integral of the electric field

$$
N^2 = \int_{-\infty}^{\infty} |E_y(x)|^2 dx,
$$

(5.4)
Figure 5.4: (Left) Calculated waveguide loss, $\alpha_{wg}$, due to absorption as a function of the interlayer thickness, $d_{il}$. (Right) Coupling coefficients for second-order gratings as a function of inter layer thickness, $d_{il}$. $\kappa_1$ and $\kappa_2$ are the coupling coefficients arising from first-order and second-order Bragg scattering, respectively. (Parameters: wavelength $\lambda = 450$ nm, duty cycle $dc = 0.3$, grating depth: $d_{gr} = 50$ nm, refractive index of gain polymer $n_p = 1.96$, refractive index of inter layer $n_{il} = 1.551$.)

and $\Delta [n^2(x, z)]$ is the perturbation in refractive index of the corrugation.

According to equation (5.3), the coupling coefficient is determined by the overlap between the electric field $E_y(x)$ and the refractive index modulation $n(x)$ of the grating. For a rectangular grating structure, the coupling coefficient for first order feedback of TE modes can be described in approximation by [18–20]

$$\kappa_1 = \frac{\Delta [n_{eff}^2]}{\lambda_{Bragg}} | \sin (2\pi dc) | \quad (5.5)$$

In second order gratings, light is coupled out perpendicularly to the surface. This form of feedback can also be viewed as another form of optical loss in the resonator. Thus, in such gratings the coupling coefficient needs to be extended by an imaginary part $i\kappa_2$ which takes these diffraction losses into account [20–22], yielding

$$\kappa_2 = \kappa_1 \frac{2\Delta [n_{eff}^2] d_{gr}}{\lambda_{Bragg}} \tan (\pi dc), \quad (5.6)$$

where $d_{gr}$ is the grating height.
Figure 5.5: Fundamental TE polarised slab mode profile $|E_y(x)|^2$ for two different structural configurations with Y80F8:20F5 as gain polymer: (top) 40 nm thick inter layer, and (bottom) 100 nm thick inter layer. Note that the shaded region represents modal penetration into ITO.

For these simulations, the upper surface of the gain polymer layer with $n_p = 1.96$ is assumed to be flat. An increasing inter layer thickness will then consequently lead to a change in the effective refractive index and has thus also a significant influence on the coupling coefficient of the DFB grating, as can be seen in the right part of Figure 5.4, in which the curves were calculated considering equations (5.5) and (5.6). A thicker interlayer increases the confinement in the gain polymer and is on the one hand beneficial for the modal losses and the amplification of the mode, according to equation (2.40). On the other hand, however, it decreases the confinement in the grating region and hence the coupling coefficient which leads to weaker feedback within the DFB resonator and weaker emission from the laser.

An aspect which has not attracted much attention in the literature is the fact that increasing device thicknesses allow the presence of more than one guided mode [12, 23]. Figure 5.6 shows both the calculated waveguide losses and the coupling coefficients for all guided modes in the discussed structure as functions of the inter layer thickness. It is shown that even for minimal interlayers, the waveguide is multimode allowing the propagation of the fun-
damental TE\textsubscript{0} mode, as well as TM\textsubscript{0}, TE\textsubscript{1} and TM\textsubscript{1}. The implication is that the spontaneous emission is coupled into these other modes, thereby reducing the efficiency of coupling to the desired mode (TE\textsubscript{0}). However, while thicker interlayers reduce the absorption losses of the TE\textsubscript{0} and TM\textsubscript{0} modes, the opposite is the case for TE\textsubscript{1} and TM\textsubscript{1}, see Figure 5.7.

![Figure 5.6: (Left) Calculated waveguide loss due to absorption for all occurring modes in dependence of the interlayer thickness: (blue) TE\textsubscript{0}, (red) TE\textsubscript{1}, (green) TM\textsubscript{0}, (black) TM\textsubscript{1}. (Right) Coupling coefficients for second order gratings in dependence of the interlayer thickness for same modes. Solid line indicates $\kappa_1$, dashed line indicates $\kappa_2$. (Parameters: wavelength $\lambda = 450$ nm, duty cycle $dc = 0.3$, grating depth $d_{gr} = 50$ nm, refractive index of interlayer $n_i = 1.551$, gain polymer layer thickness $d_p = 180$ nm.)](image_url)

In summary, an increasing interlayer thickness does reduce the optical losses due to absorption as it shifts the mode away from the lossy ITO layers into the gain material. But at the same time it leads to weaker feedback, making a trade-off between absorption and feedback unavoidable.

### 5.3.2 Refractive Index of Interlayer

The next sections are going to consider the effects on losses and confinement from the point of view of the refractive indices of the interlayer and the gain material, and as findings in the later part of this Chapter show, they can have a significant impact on the overall threshold of the laser device.

Apart from the interlayer thickness, the influence of the refractive index
Figure 5.7: Modal profiles of $\text{TE}_0$ (top) and $\text{TE}_1$ (bottom) modes. Here, $\text{TE}_1$ has a greater distribution in lossy ITO layers which contributes to higher overall waveguide losses. Shaded regions indicate parts of the modes confined in ITO layers.

of the interlayer, $n_i$, on the waveguide losses has also been investigated. The results of this study are shown in Figure 5.8. The refractive index in this simulation was varied over a range that is covered by commercially available PDT/PSS materials [24]. PDT/PSS is a well studied hole injection material which is commonly used in OLEDs, and might potentially be used in an electrically driven polymer laser, too. If the refractive index of the interlayer is increased by only 0.1, the waveguide losses due to absorption
increase considerably by 60%. This is caused by a broader modal intensity profile and as a result, a higher confinement in the lossy electrode, as it is depicted in Figure 5.9.

![Figure 5.8: (Left) Calculated waveguide loss, $\alpha_{wg}$, due to absorption as a function of the interlayer refractive index, $n_{il}$. (Right) Coupling coefficients for second-order gratings as a function of interlayer refractive indices, $n_{il}$. (Parameters: wavelength $\lambda = 450$ nm, duty cycle $dc = 0.3$, grating depth $d_{gr} = 50$ nm, refractive index of gain polymer $n_p = 1.96$, optical path length of interlayer $n_{il}d_{il} \approx 108.6$ nm.)](image)

The right part of Figure 5.8 shows the calculated coupling coefficient’s dependence on the refractive index of the interlayer. As in the cases before, the grating has a duty cycle of 0.3 and a modulation depth of 50 nm. In order to allow for comparability, the interlayer thickness is slightly adjusted to the change in refractive index such that the optical path length, $n_{il}d_{il}$, is fixed to 108.6 nm. For all values, the real part of the coupling coefficient, $\kappa_1$, is in the order of thousand per cm, indicating a strong index coupling component. In the investigated spectrum of refractive indices, $\kappa_1$ is at least 55 times larger than $\kappa_2$. The laser based on this multilayer structure should therefore show typical behaviour of index coupling [25], featuring a clear stop band and a single laser peak on the short wavelength side of the stop band. Furthermore the surface emission induces additional resonator losses, $\alpha_{res} = 2\kappa_2$, in the order of 25 to 45 cm$^{-1}$. 

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Figure 5.9: Fundamental TE polarised slab mode profile $|E_y(x)|^2$ for two different structural configurations with Y80F8:20F5 as gain polymer and interlayer refractive indices of (top) 1.57 and (bottom) 1.47.

5.3.3 Refractive Index of Gain Polymer Layer

The third parameter investigated is the refractive index of the gain polymer, $n_p$, and its influence on the waveguide losses and coupling coefficients. The left part of Figure 5.10 shows the calculated losses. Again, the range of refractive indices was chosen to cover those of available materials, such as PFO ($n = 1.76$) and Y80F8:20F5 ($n = 1.96$). If Y80F8:20F5 is used instead of PFO, i.e. if the refractive index of the gain polymer is increased by 0.2, the waveguide loss decreases drastically by a factor of more than 5. This can be explained by the significant change in the modal intensity profile shown in Figure 5.11. While the intensity profile exhibits two peaks for $n_p = 1.76$, one in the grating region and one in the gain polymer layer, an index of 1.96 leads to a modal profile that is much narrower and strongly confined in the gain polymer. Hence, the result is a smaller overlap with the lossy ITO as depicted in Figure 5.11.

Figure 5.10 (right) shows the coupling coefficient’s dependence on the gain polymer refractive index. As in the previous case, the film thickness is adjusted to the refractive index such that the optical path length is fixed
to 352.8 nm. For low refractive indices $\kappa_1$ is an order of magnitude larger than $\kappa_2$ but this difference increases to nearly two orders of magnitude for refractive indices around 2. The contribution of gain coupling is therefore small and the multilayer lasers should exhibit index coupling behaviour with a clear photonic stop band. The width of a stop band is $\Delta \lambda \equiv 2\kappa c$ [26]. Due to the enormous coupling coefficient, this should be between 7 and 37 nm. However, due to the $\kappa_2$ values between 12 and 490 cm$^{-1}$, this stop band will not be well pronounced. Additionally to the waveguide losses due to absorption, the cavity losses induced by surface emission amount to the order of 24 to 980 cm$^{-1}$.

The results suggest that additionally to the thickness and refractive index of the interlayer, the refractive index of the gain polymer strongly influences the mode confinement in the absorptive electrode. Increasing the refractive index of the gain polymer leads generally to a smaller fraction of the propagating mode in the ITO and also to a steeper decay of the waveguide losses as a function of the interlayer thickness, as shown in Figure 5.12. Thus, a higher refractive index of the gain polymer allows to reduce the thickness of
Figure 5.11: Fundamental TE polarised slab mode profile $|E_y(x)|^2$ for two different structural configurations: (top) Y80F8:20F5 with a refractive index of 1.96, and (bottom) PFO with a refractive index of 1.76.

Figure 5.12: Waveguide loss in dependence of interlayer thickness for a series of gain polymer refractive indices. Optical path lengths of the respective gain polymer layers were fixed to $n_y d_y \approx 352.8$ nm.

the interlayer as well as the thickness of the gain polymer itself (regarding a fixed optical path length), and hence the overall thickness of the polymer laser device.

These findings show that the increase of the refractive index of the gain
polymer is a promising approach towards polymer laser diodes. One possibility is to use side-chains as a means of more dense packing as in the case of Y80F8:20F5.

5.4 Device Fabrication

Following the simulation result from section 5.3.2, a PDT/PSS version is required which exhibits a refractive index as low as possible with at the same time low absorption in the emission spectrum of the gain polymer. The conductive material Clevios P VP CH 8000 was therefore chosen as the most suitable alternative with \( n_\text{il} = 1.551 \) and \( \alpha_\text{il} = 977 \text{ cm}^{-1} \) at 450 nm [27]. It is an aqueous dispersion of poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) in a weight ratio of 1:20 [28]. In the experiments for this work, SiO\(_2\) substrates or ITO-coated SiO\(_2\) substrates with an ITO thickness of 70 nm and a refractive index of \( n_{\text{ITO}} = 2.03 \) at 450 nm were used. 1D DFB resonators were fabricated into these ITO films by the Centre for Integrated Photonics (CIP). The gratings were designed to feature a periodicity of 270 nm with a duty cycle of 30%. The modulation depth of these gratings was about 50 nm as determined by atomic force microscopy (AFM). Figure 5.13 shows high resolution scanning electron microscopy (SEM) images of the ITO gratings. Grating (left) has a modulation period of 270 nm, grating (right) has a periodicity of 290 nm.

The interlayer was spin cast on top from a volume-reduced solution which allowed us to achieve film thicknesses between 60 and 320 nm. Y80F8:20F5 was used as gain polymer due to its promising characteristics such as high mobility \( (3.7 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1}\text{s}^{-1}) \), high photoluminescence quantum efficiency \( (70\pm5\%) \), and its high refractive index \( (n_p = 1.96) \) [29]. The Y80F8:20F5 films were \( \sim 180 \text{ nm} \) thick, and the interlayer film thicknesses were systemat-
Figure 5.13: SEM images of 1D ITO gratings with (left) $\Lambda = 270$ nm, and (right) $\Lambda = 290$ nm.

Figure 5.14: Schematic architecture of the ITO DFB laser device and AFM images of the ITO grating (~50 nm) and the air-polymer corrugation on top (~5 nm).

ically increased. Figure 5.14 shows the schematic structure of the DFB laser as well as AFM images of the ITO grating and the polymer-air corrugation (~5 nm). This is rather a minor corrugation compared to previous findings [30], and is an order of magnitude smaller than the grating modulation depth.

In Figure 5.15, the absorption spectra of the PEDT/PSS dispersion and of Y80F8:20F5 as well as its ASE spectrum are shown. The ASE emission has a FWHM of about 5 nm centred at 449 nm. As can be seen from the absorption
5.5 Emission Characteristics

To experimentally investigate the influence of ITO on the waveguiding characteristics, multilayer waveguide samples in two different configurations were fabricated. Both sets of samples were based on SiO$_2$ substrates and had the same interlayer thickness (~100 nm) and gain polymer thickness (~180 nm), but one included a 70 nm thick ITO layer. In all samples gain narrowing coincided with the 0-1 transition, consistent with the four-level gain model described in Section 2.3. This is interesting insofar as recent experiments have shown a blueshift of PFO ASE emission for similar multilayer structures [23]. Heliotis attributed this behaviour to a change in the PFO morphology when spin-coated on top of the PDT/PSS interlayer.

Figure 5.16 shows the pump fluence dependence of (blue) the emission intensity at ASE wavelength for two different multilayer configurations. The spectrum, the PEDT/PSS interlayer is not absorbing in the spectral range of the optical gain and hence does not contribute to absorption losses.
Figure 5.16: (Blue) ASE peak intensity dependence on pump fluence. Note the change of slope upon the onset of ASE and the decrease of slope at high intensities. The dashed lines are guides to the eye. (Red) FWHM of ASE spectra plotted versus pump fluence. Measurements were performed on multilayer waveguides (a) in the absence, and (b) in the presence of ITO.

double-logarithmic scale allows one to observe ASE as a change of slope from a linear dependence on the pump fluence to a superlinear dependence. In the absence of ITO the threshold fluence is $\sim 43 \mu J/cm^2/pulse$ which corresponds to a power density of $\sim 1.9$ kW/cm$^2$. However, the corresponding threshold value in the presence of ITO was found to be $\sim 120 \mu J/cm^2/pulse$ or 5.2 kW/cm$^2$. At pump intensities higher than 110 $\mu J/cm^2$ or 4.8 kW/cm$^2$ (ITO absent), 260 $\mu J/cm^2$ or 11.3 kW/cm$^2$ (ITO present) respectively, the intensity dependence becomes linear again. This typical s-shape is described in Chapter 3.5. To determine the threshold value from the spectral evolution (Figure 5.17), the width of the ASE spectrum was extracted and plotted versus pump fluence in semi-logarithmic fashion. Then, the data was fitted with the sigmoidal function describing the dependence of the FWHM on the pump fluence [31]:

$$
\Delta \lambda_{\text{ASE}}(F) = \frac{A1 - A2}{1 + (F/F_0)^p} + A2
$$

(5.7)

where $F$ is the pump fluence per pulse, $A1$ and $A2$ are maximum and minimum FWHM, respectively. $F_0$ is the pump fluence at FWHM = $(A1+A2)/2$,
and $p$ is a measure of the steepness of the function. The ASE threshold was extracted from the intersection of the upper linewidth limit with the tangent at the turning point of the sigmoidal curve (Figure 5.16). In the absence of ITO, the value deduced from this approach is identical within errors with the value determined from the change of slope in the pump intensity dependence. In the presence of ITO, this value still corresponds well at a threshold of $143 \, \mu J/cm^2$ ($\sim 6.2 \, kW/cm^2$) for the observation of ASE.

Comparing the input fluence dependence of output signal and FWHM two things need to be noted. First, the difference of the spontaneous emission factors indicated in Figure 5.16 by $\beta$. According to the theory of Suematsu and Furuya [32, 33], the spontaneous emission factor of an ASE mode is defined as

$$
\beta_i = \frac{\text{radiation energy coupled into } i\text{th ASE mode}}{\text{total radiation energy}} \approx \Gamma_i \frac{\lambda_{ASE}^4}{4\pi^2 n_{eff}^3 V \Delta \lambda_{ASE}},
$$

where $\Gamma_i$ is the confinement factor in the gain polymer layer of the $i$th ASE mode, $V$ is the volume of the pumped region, and $\Delta \lambda_{ASE}$ is the FWHM of the ASE emission spectrum. Solving this equation with the respective parameters for the two samples discussed above yields spontaneous emission factors of $4.6 \cdot 10^{-7}$ for the SiO$_2$ device, and $1.8 \cdot 10^{-7}$ in the ITO case. However, the experimental values determined from Figure 5.16 are 0.65, 0.38 respectively. The discrepancy of six orders of magnitude shows that even the employed setup for ASE measurements (described in Section 3.5) did not only collect waveguided ASE modes but also a large number of additional modes, including top emitting radiation. Reasons for this are complex and can be found in factors such as the relatively large stripe width ($\sim 100-200 \, \mu m$) of the pumped region or the notoriously poor quality of the facets which both
increase the collected emission from the lateral pump area. For example, a stripe width of 100 µm already leads to several hundred modes. The concept of β in inorganic waveguides assumes that there is lateral confinement (e.g. channel or ridge waveguides). However, such waveguide structures are still very difficult to realise with conjugated polymers and thus, collecting ASE in a single mode is still a problem to be solved.

The second thing to be noted is the development of FWHM for high pump intensities. While in the absence of ITO, the spectral evolution follows the common pattern and collapses to about 5 nm, the corresponding ITO samples show a different ASE behaviour. Gain narrowing in all investigated ITO samples leveled off at around 10 nm. Multilayer structures will in general change the emission profiles; depending on the quality of the facet one could be seeing several simultaneous ASE events from adjacent waveguides as the pump beam is quite wide. The spectral narrowing shows that there is clearly ASE, but more experimental work with a more suitable set-up would need to be done to explain this behaviour. The spectral results from the edge emitted ASE discussed above for both multilayer waveguides are shown in semi-logarithmic fashion in Figure 5.17.

In order to distinguish between the individual contributions of the different layers to the waveguide loss of DFB devices, three samples were modelled with increasing number of layers, as can be seen in Figure 5.18. First, a simple slab waveguide on a SiO₂ substrate was fabricated, then a monolayer laser device on ITO was made, and finally a PEDT/PSS (Clevios P VP CH 8000) was added.

The losses of the basic slab waveguide can be neglected since Y80F8:20F5 does not absorb at 450 nm. However, there are several reports on total losses of polyfluorene waveguides which include additional losses such as scattering, and the values reported ranged between 3 and 15 cm⁻¹ [3, 34–38], and
Figure 5.17: ASE measured at the edge of the waveguides. Left figure shows the spectral development on a SiO$_2$ substrate for pump fluences of (blue) 25 and (red) 248 $\mu$J/cm$^2$. Right figure shows emission spectra on an ITO sample for pump fluences of (blue) 103 and 790 $\mu$J/cm$^2$. While the FWHM collapses to about 4 nm in the SiO$_2$ case, it levels off at more than 10 nm for ITO substrates.

Figure 5.18: Layer configurations of the investigated multilayer devices.

Yap et al. have reported total losses of Y80F8:20F5 waveguides as low as 1.8 cm$^{-1}$ [29]. For the slab waveguide fabricated on top of ITO, the absorption loss increased to $\sim$1330 cm$^{-1}$. This is a rather high value compared to previous reports [10, 39], which is due to a very high absorption coefficient of the employed ITO itself of $\sim$6500 cm$^{-1}$. Finally, a multilayer structure...
with an 100 nm thick interlayer was fabricated (see Figure 5.18), in order to reduce the modal penetration in the absorptive ITO. As a consequence, the absorption losses decreased dramatically by a factor of 10 to 124 cm$^{-1}$.

Time-resolved photoluminescence experiments were used to measure the exciton lifetime in Y80F8:20F5 films both on SiO$_2$ and ITO substrates. For these measurements time-resolved single-photon counting (TRSPC) was employed using a diode laser ($\lambda = 404$ nm, FWHM $\sim$230 ps), IHB photon detection module, and IBH Datastation hub (all Jobin Yvon). Figure 5.19 shows the PL decay curves for the two samples. All curves could be fitted with reasonable accuracy to monoexponential decays, from which the singlet exciton lifetime $\tau_R$ could be estimated by calculating the $1/e$ decay time. It was found that $\tau_R$ on both substrates was around 490 ps, and hence ITO does not affect the exciton lifetime - at least not in the present structures.
5.6 Lasing on Conductive DFB Gratings

The previous sections employed numerical simulations to establish design rules for multilayer lasers with conducting DFB gratings, and studied the influence of ITO on the optical performance of Y80F8:20F5. This section shows that a multilayer architecture with a conducting DFB resonator can be realised and might offer a route towards polymer laser diodes. Results of a study of optically pumped lasing in the blue spectral region are reported.

Figure 5.20 shows the emission spectrum of a multilayer second order DFB laser measured parallel to the substrate normal, for energies below and above threshold. The laser was based on an ITO substrate with $\Lambda = 270$ nm and a modulation depth of 50 nm. The Y80F8:20F5 film was 150 nm thick, and the interlayer film 70 nm respectively. Even with such thin films, the device was able to support four modes, the fundamental TE and TM modes as well as those of first order. The sample was excited by the frequency-tripled Nd:YAG laser, focused to circular spot of 240 $\mu$m.

At a pump pulse fluence of 25 $\mu$J/cm$^2$ the emission is strongly modulated.
by Bragg scattering with a pronounced dip at 449.1 nm. Since a substantial fraction of the waveguided light is coupled out of the surface in second order DFB lasers, this dip can be attributed to a photonic stop band, a range of wavelengths for which propagation is suppressed by the DFB. This stop band spanned from 447.8 nm to about 449.8 nm. At a fluence of 31 µJ/cm² however, the spectrum collapsed to a narrow peak located within the stop band but on the short wavelength side. This indicates that a form of coupling was in place that included contributions of index as well as gain coupled, and is refered to as complex coupling. This observation is inconsistent with the model of pure index coupling which would predict lasing on one of the band edges. As noted in Section 2.7.1, gain modulation cannot be neglected in shallow gratings. Such complex coupling can shift a resonance of the DFB resonator within the stop band [40]. At 77 µJ/cm² this laser peak dominates the spectrum with a FWHM of 0.5 nm.

Figure 5.21 shows the laser characteristics of the SiO₂ and ITO grating samples as a function of the pump energy per pulse for devices with an interlayer thickness of ~80 nm (d_p = 175 nm). On both samples laser thresholds could be observed as indicated by a sharp change of slope of the emitted energy at lasing wavelength, followed by a linear increase in output with increasing pump energy. For pump energies below threshold broad spontaneous emission spectra were recorded which were modulated by Bragg scattering. The evolution of the emission spectrum for the ITO grating device is shown in the inset. Beyond threshold, a narrow peak arose at 457 nm with a FWHM of 1.5 nm which increased with pump intensity to around 2 nm. For the SiO₂ grating sample, a threshold energy of 10 nJ/pulse (14.6 µJ/cm² or 0.6 kW/cm²) was obtained, which increased to 41 nJ/pulse (58 µJ/cm² or 2.5 kW/cm²) for the ITO grating device.

The slope efficiencies were calculated from the input/output energies above
threshold and were 0.5% and 0.2% for the SiO$_2$ and ITO gratings, respectively. The higher threshold and lower slope efficiency of the ITO device are expected to be different since the structure itself exhibits a quite diverse optical environment compared to the SiO$_2$ device. Furthermore, the fact that the resonance wavelength of the ITO device was further away from the centre of the gain peak also leads to a worse performance.

### 5.7 Considerations for Electrical Pumping

The results of these measurements allow one to estimate the lasing threshold required for electrically pumped lasers. The lowest threshold fluence of an multilayer ITO laser measured during the course of this work was $31 \ \mu\text{J/cm}^2$ for optical excitation at 355 nm or $5.6 \times 10^{-19} \ \text{J} \ (3.49 \ \text{eV})$. This threshold fluence corresponds to $5.54 \times 10^{13}$ input photons of which 93.1% will be absorbed in the gain polymer ($\alpha_p = 1.53 \times 10^5 \ \text{cm}^{-1}$). Taking into account the PLQE of the Y80F8:20F5 film on top of ITO and the interlayer, $\sim 46\%$, the density of emitted photons at lasing threshold can be estimated
as $2.55 \times 10^{13}$ cm$^{-2}$. This number represents the minimum photon density necessary for lasing oscillation and would be generated electrically in a polymer laser diode. Note that the following calculations should only be regarded as qualitative estimates since the studied device only included one electrode. The current density at threshold could then be expressed by

$$J_{\text{thr}} = \frac{S_{\text{thr}}q\zeta}{\eta_{\text{int}}\tau_R}$$  \hspace{1cm} (5.9)

where $S_{\text{thr}}$ is the photon density at threshold, $\tau_R$ is the radiative lifetime of the excited state (cf. Section 2.3), $q$ is the electrical charge, $\zeta$ is a correction factor for annihilation processes, and $\eta_{\text{int}}$ is the internal quantum efficiency, and given by [41]

$$\eta_{\text{int}} = \gamma_{\text{eh}} r_{st}\text{PLQE}$$  \hspace{1cm} (5.10)

where $\gamma_{\text{eh}}$ is the efficiency of electron-hole capture within the gain polymer layer, and $r_{st}$ is the fraction of excitons that are generated as singlets. The value of $\gamma_{\text{eh}}$ is close to unity [42]. The second term in the product is the singlet-to-triplet ratio. It has been assumed that this ratio is set by spin statistics whereby three triplets are formed for every singlet. However, there have also been studies which suggest that the fraction of singlet excitons in conjugated polymers could be higher than 25% [43–46]. Assuming a singlet fraction of 25% and $\gamma_{\text{eh}} \sim 1$, the internal quantum efficiency yields 11.5%. The estimate of $\zeta = 5$ is based on the results reported by Gärtnner et al. who have simulated the effect of various annihilation processes in a structure of comparable gain polymer thickness [47]. Together with the radiative lifetime of Y80F8:20F5 ($\tau_R = 490$ ps), an estimate of the current density at threshold yields therefore at least 360 kA/cm$^2$. Current densities of the order of $10^1$-$10^2$ kA/cm$^2$ have been reported in organic devices operating in steady state and pulsed modes [48, 49]. Furthermore, current densities in the order of 0.1
to 1 kA/cm² have been demonstrated by several groups working on OLED devices which had overall thicknesses of some 100 nm [1, 48, 50–52].

Any practical application of multilayer polymer lasers is limited by the lifetime of the gain polymer. Results reported in recent years suggest that photo degeneration in dye lasers, which is probably caused by the local heating of the layer by the pump pulse, contribute to the decrease of the output intensity [53–57]. The stability and thus the operating lifetime of the ITO DFB lasers was investigated by monitoring the decrease of the output intensity as a function of the number of pump pulses. As with all previous measurements, the polymer laser devices were kept in atmosphere. For this experiment, the operating lifetime is defined as the number of pulses after which the initial output intensity drops to 50%.

In comparison with pure dye lasers based on Rhodamine 6G, DCM and Pyrromethene 567 [53–57], both multilayer polymer lasers exhibited a much greater lifetime (> 1-2 orders of magnitude), thus indicating a high stability of polyfluorene materials. This result is confirmed by the results of polyfluorene laser measurements conducted in a vacuum chamber (∼10⁻⁴ mbar), which have shown lifetimes of ∼8×10⁶ at a pump energy density twice the threshold [23]. On the other hand Voss et al. have shown that a DFB laser based on a poly(methyl methacrylate) (PMMA) film doped with Rhodamine B can also exhibit a lifetime of up to 3.5×10⁵ pulses (τ = 540 ps, ν = 3 kHz) [58]. Figure 5.22 shows the data of two operating lifetime measurements, for samples with a SiO₂ and an ITO grating respectively. It was found that at a pump fluence per pulse of 5.43 µJ/cm², twice the threshold, the SiO₂ laser device can emit ∼3×10⁴ pulses until the output signal drops to 50% of its initial value. However, when a comparable multilayer sample employs an ITO DFB grating and is also investigated at twice the threshold, or 86 µJ/cm², the laser degrades more rapidly and the lifetime drops to
Figure 5.22: Output pulse intensity from Y80F8:20F5 lasers as a function of pump pulse number at two times threshold for (blue) SiO₂ and (green) ITO grating substrates. The red lines are exponential fits used to determine the operating lifetimes. $\tau = 23$ ns, $\nu = 10$ Hz, $T = 21$ °C.

$\sim 10^4$ pulses. Besides photo-oxidation, reactive indium cations diffusing out of the ITO into the interlayer and the gain polymer [59], are shortening the device lifetime. It has to be noted that during these measurements neither linewidth broadening nor wavelength shifting could be observed.
5.8 Summary

This chapter reported a systematic numerical study of the optical environment on the performance of blue-emitting lasers on conducting DFB resonators, which was followed by a demonstration of optically pumped polymer lasers based on ITO gratings. Findings of the simulations suggest that in order to overcome limiting factors set by the presence of electrode materials, a combination of high refractive index gain polymers and low refractive (conducting) interlayers is desirable. Experimental data was used to verify this approach. Laser emission was measured under optical excitation at 355 nm using a frequency-tripled Nd:YAG laser.

The results presented here extend the variety of approaches towards polymer laser diodes. Past research on polymer laser devices was focused on high gain [60], low thresholds [8, 13, 61, 62], and high mobilities [7, 29]. Over the last years progress could be seen on all these fields. However, charge carrier mobilities are still not high enough to allow organic layers of several 100 nm. Conclusions from the conducted ASE measurements and simulations presented in this thesis are that a high refractive index of the gain polymer is fundamental importance in order to overcome absorption losses due to an ITO contact and limit the overall device thickness to realistic dimensions.
Bibliography


Chapter 6

Non-Periodic Circular Bragg Resonators

6.1 Introduction

As mentioned in the preceding chapters, research in the field of conjugated polymer lasers is partly driven by the effort to realise electrically pumped laser action with devices based on such materials. As was pointed out in the introduction to this thesis, a major challenge towards this goal is to further reduce the threshold fluence required for laser action as this is expected to directly translate into a reduction in the current density required under electrical excitation. As a consequence there has been much interest in exploring different resonator concepts, including microcavities [1], microrings [2], microdroplets [3] and DFB structures [4]. Amongst these, DFB resonators have attracted the most interest due to a combination of low threshold operation and single mode lasing for moderate excitation intensities. The concept of organic DFB lasers has evolved from an, initially, one-dimensional grating structure [4] such as those investigated in Chapters 4 and 5, to DFBs that employ feedback in more than one direction. These include structures with two-dimensional feedback that consist of two-orthogonally superposed linear gratings [5], photonic crystal lattices [6], and circular structures that provide feedback in all directions within their plane [7–9].
Circular Bragg resonators (CBRs) represent an interesting and very useful class of resonators that, among other attributes, can provide very low thresholds and an ultra-small modal volume with high $Q$ operation, and that naturally produce well-defined circularly-symmetric outputs [7–17]. Originally demonstrated in the field of inorganic semiconductor lasers [10–13], several polymer-based structures, operating largely in the green and red spectral region, have recently been reported [7–9]. CBRs support circular modes, with the electric field amplitudes for these modes determined from solutions of the Helmholtz equation in cylindrical coordinates. As with conventional linear DFB resonators, the interface between low and high refractive indices should be positioned in such a way that the partial reflections from each successive spatial modulation add in phase [10], as described in Chapter 2.7. In the case of CBRs, the optimal grating design would then ideally employ a non-periodic modulation profile in order to closely match the nulls/maxima of the corresponding $m$th-order Bessel function [14, 16, 18]. Lower lasing thresholds, improved mode discrimination and, in particular, a higher $Q$ factor for the resonator might then be expected [16].

This chapter explains the design rules for the CBR substrates with respect to desired emission wavelength and refractive index of the gain material. Atomic force microscopy and scanning electron microscopy (SEM) are used to characterise the substrate surface and quality. Finally, a detailed study of the influence of the grating characteristics as well as the modal properties of the output beam are given.

### 6.2 Resonator Design and Fabrication

Figure 6.1(a) illustrates the grating design used for the work on CBR lasers, also shown for comparison (Figure 6.1(b)) is the profile used to date for other polymer based circular grating studies [7–9]. The design strategy is illustrated in Figure 6.1(c) where the refractive index modulation, shown as the grating profile height, is superimposed with the radial profile of the $J_0$
Figure 6.1: Schematic cross-sections of resonator structures with polymer overlayers (a) Present work (b) Conventional CBR design [7–9]. (c) Illustration of the design strategy used in the present work showing height profile (and hence refractive index modulation) (solid line) together with the radial profile of the $J_0$ Bessel function (dashed line).

Bessel function.

The first interface (at $\rho_0$) goes from high to low refractive index, for polymer lasers the grooves have a high refractive index, and ridges have a low refractive index since the substrates (i.e. SiO$_2$) used have a lower refractive index than the polymer (contrary to the approach used previously in inorganic lasers). This layout provides more gain in the centre region. Further interfaces were placed in such a way that a change

- from low to high refractive index occurred at the first extremum of $J_m(\rho)$, with $\rho > \rho_0$,

- and from high to low refractive index at the zeroes of $J_m(\rho)$, leaving out one zero and one extremum per grating interval (see Figure 6.1(c)).

This sequence leads to a surface-emitting structure with in-plane feedback via second-order Bragg scattering and surface emission via first-second order Bragg scattering. A series of resonator structures were fabricated with two parameter variations, namely grating period and duty cycle (groove/period ratio).
The gratings are etched into $10 \times 10 \text{ mm}^2$ SiO$_2$ (600 nm) on silicon substrates, with ten different laser resonators per substrate. The individual resonators have an outer diameter of 160 $\mu$m with a grating depth of $70 \text{ nm} \pm 6 \text{ nm}$. This is limited by the e-beam system - there are $128000 \times 128000$ pixels that can be written by the system. The highest resolution is 1.25 nm, which gives an area of $160 \mu m \times 160 \mu m$. The grating 'period' is varied between 260 and 290 nm with a fixed duty cycle of 75% on one substrate and on the second, the duty cycle is varied from 16.7 to 83.3% while the 'period' is kept fixed at 280 nm. The gratings are fabricated at the Physikalisch-Technische Bundesanstalt in Braunschweig, Germany. An electron-beam (Leica 5000+ electron-beam writer) lithography based lift-off process is used to prepare a chromium etch mask on top of the SiO$_2$ prior to etching with CHF$_3$. The circular grating structures always fit within the whole-field electron-beam exposure area such that stitching can be avoided. Images of one of the CBR structures are shown in Figure 6.2 (SEM scan performed by the PTB, AFM scan by Dr. Patrick Howe) and demonstrate the exceptional quality of the gratings produced. To our knowledge this is the first time that CBR structures have been successfully used for blue emission lasers.

All gratings are designed to provide both distributed feedback and outcoupling of the propagating mode via first- and second-order Bragg scattering.
Figure 6.3: (a) Atomic force microscopy image of the centre portion of a nominally 100 nm deep CBR grating. (b) Cross-section of the same resonator measured along the white line in (a). The grating period is $\Lambda = 260$ nm, the duty cycle is designed to be 75%.

Figure 6.3(a) shows an AFM scan of one of the investigated CBR gratings, which is taken in a $5 \times 5 \mu m^2$ region in the centre of the grating. The inner region of this grating is designed to have a radius of 99.5 nm. Figure 6.3(b) shows the cross section profile of the very same grating. The nominal depth of the grating is 100 nm but as the profile shows it exhibits a depth of 110 nm with a variation of $\sim 5$ nm. Note that tip convolution is the reason for the apparent shallowness in the centre disk and the fact that the grating profile digresses from the ideal square-wave shape\(^1\). The same situation was also found in other grating structures for polymer lasers [9, 19].

### 6.3 Experimental Details

For this study, the statistical copolymer BN-PFO was used as gain material. The laser structures were fabricated by spin-coating the BN-PFO solution on top of the etched SiO$_2$ gratings to form thin films of thicknesses between 105 and 150 nm. The film thicknesses were measured in unpatterned regions

\(^1\)Every data point in an AFM image represents a spatial convolution of the shape of the tip and the shape of the feature imaged. As long as the tip is much sharper than the feature, the true edge profile of the feature is represented. However, when the feature is sharper than the tip, the image will be dominated by the shape of the tip.
of the substrate using a Tencor surface profilometer. The samples were then optically-pumped at 355 nm using the frequency-tripled Q-switched Nd:YAG laser (c.f. Section 3.6); the pumping scheme is shown in Figure 6.4. The output energy per pulse of the pump laser is varied using calibrated neutral density filters and monitored using a Scientech Vector High Resolution Pyroelectric Detector P09 a. The pump beam is cleaned up using an iris, and then expanded again by a telescopic lens arrangement to fill out the entrance of the microscope objective which focuses the beam onto the polymer surface of the laser sample. The sample itself is mount on an xyz-stage. The pump spot radius can be varied between 8 and 50 µm by translating the sample along the optical axis toward and away from the microscope objective. The spectral emission of the polymer laser is collected by the same microscope objective. The collimated emission is then reflected into a lens by a pellicle beamsplitter, and focused into an optical fibre which was connected to a spectrometer (details are given in Chapter 3.5). The optical monitoring system described in Chapter 3.6 is used to accurately control the pump spot localisation on the gratings. A Gentec WinCamD beam profiler was used to measure the pump spot radii and image the surface emitting laser emission. For the latter, the sample is pumped at an
incident angle of 20°, so that the emission can be measured without using any additional optics.

6.4 Influence of Grating Characteristics

The lasing wavelength in a polymer DFB laser may be selected via adjustment of the grating parameters and/or film thickness. The first set of investigated laser devices consists of ten resonators for which the grating ‘period’ varies whilst the duty cycle and BN-PFO film thickness are held fixed. Figure 6.5 shows the lasing wavelength as a function of grating ‘period’, covering a spectral range of 27 nm, from 437 to 464 nm. The observed linear relationship can be described in terms of the Bragg condition for second order gratings [20],

\[ \lambda_{\text{Bragg}} \approx n_{\text{eff}} \Lambda, \]  

(6.1)

which is the special form of equation (2.45). A fit to the data yields \( n_{\text{eff}} = 1.64 \), which together with the BN-PFO refractive index (\( n = 1.96 \) at 450 nm) leads to a confinement factor of around 84%.

Figure 6.5 also presents the spectral variation of the BN-PFO CBR laser threshold energy together with the corresponding PL and ASE spectra. For this series of CBR structures the lowest threshold pulse energy is 110 pJ (corresponds to a pulse fluence of 7 \( \mu J/cm^2 \), with pump radius \( r_{\text{pump}} = 22 \mu m, \tau_{\text{pulse}} = 23 \text{ ns} \)) and occurs for structures lasing around 450 nm which coincides with the peak of the ASE spectrum, in close proximity to the (0-1) PL emission. Similar results for broadband-tuning have previously been reported for BN-PFO lasers based on other DFB structures [21, 22].

The dependence of the laser emission wavelength on the grating duty cycle is shown in Figure 6.6. The duty cycle or groove-to-period ratio is varied between 16.7% and 83.3% while the grating period and polymer film thickness are kept constant at 280 nm and \( \sim 135 \) nm respectively. It is found that this variation in the grating profile can have a significant impact on the
Figure 6.5: BN-PFO CBR lasing characteristics: (Top) Laser wavelength as a function of grating ‘period’ (fixed duty cycle and BN-PFO film thickness $\sim 135$ nm). The solid line shows a fit using the Bragg condition for second order gratings. (Bottom) Threshold energies for laser oscillation as a function of emission wavelength (data points). The solid curve shows the BN-PFO PL spectrum and the dashed curve shows the corresponding ASE spectrum.

effective refractive index and hence the lasing wavelength. Such behaviour can be understood by considering again the Bragg condition (2.45) which states that the emission wavelength is a product of the grating period and the effective refractive index. For further clarification Figure 6.7 illustrates the influence of the duty cycle on the ratio of polymer per period. It shows that a laser device with a duty cycle of 75% (a) contains a much greater amount of high index gain material per period than one with a duty cycle of only 33% (b), and thus has a higher effective refractive index. Over the range of studied duty cycles the effective refractive index can be altered between 1.6 and 1.625, and hence the laser emission wavelength can be tuned
Figure 6.6: Laser wavelength as a function of duty cycle with same grating ‘period’. Right axis shows results converted into effective refractive index according to the Bragg condition (2.45).

![Figure 6.6: Laser wavelength as a function of duty cycle with same grating ‘period’. Right axis shows results converted into effective refractive index according to the Bragg condition (2.45).](image1)

Figure 6.7: A comparison between two gratings with same period but different duty cycle. It illustrates that a high duty cycle, here 75%, leads to a higher amount of high index gain material per unit (period), and thus increases the effective refractive index of the device.

![Figure 6.7: A comparison between two gratings with same period but different duty cycle. It illustrates that a high duty cycle, here 75%, leads to a higher amount of high index gain material per unit (period), and thus increases the effective refractive index of the device.](image2)

from 448 to 456 nm. Laser oscillation is obtained at long wavelengths (high $n_{\text{eff}}$) for large duty cycles and decreases gradually for smaller duty cycles.

Previous studies of polymer CBRs have mostly employed uniform pumping of the grating structure [7], or used a large pump beam radius [9]. Recently, Turnbull et al. investigated the effect of photopumping strongly localised to the centre of the grating and found that it first led to a significant reduction of the laser threshold energy and an increase in output efficiency [23]. But for pump spot radii below $\sim 34 \mu m$ the laser threshold energy did not reduce any further. Translated into fluence (energy per area), this implies an ex-
Table 6.1: Overview of the performance of a range of polymer lasers based on CBRs. References for the literature results are given below the table. The bottom line shows results as presented here.

<table>
<thead>
<tr>
<th>Gain polymer</th>
<th>Lasing wavelength</th>
<th>Grating period</th>
<th>Threshold fluence</th>
<th>Pump pulse duration</th>
<th>FWHM</th>
<th>Quality factor</th>
</tr>
</thead>
<tbody>
<tr>
<td>aMeLPPP</td>
<td>494 (nm)</td>
<td>325 (nm)</td>
<td>600 (µJ/cm²/pulse)</td>
<td>20 (ns)</td>
<td>0.7</td>
<td>7057</td>
</tr>
<tr>
<td>bMeLPPP</td>
<td>495 (nm)</td>
<td>318 (nm)</td>
<td>64 (µJ/cm²/pulse)</td>
<td>20 (ns)</td>
<td>1.6</td>
<td>3094</td>
</tr>
<tr>
<td>cMEH-PPV</td>
<td>632 (nm)</td>
<td>400 (nm)</td>
<td>11 (µJ/cm²/pulse)</td>
<td>1 (ns)</td>
<td>7</td>
<td>903</td>
</tr>
<tr>
<td>dMEH-PPV</td>
<td>618 (nm)</td>
<td>400 (nm)</td>
<td>107 (µJ/cm²/pulse)</td>
<td>1 (ns)</td>
<td>10</td>
<td>618</td>
</tr>
<tr>
<td>BN-PFO</td>
<td>450 (nm)</td>
<td>276 (nm)</td>
<td>1.2 (µJ/cm²/pulse)</td>
<td>23 (ns)</td>
<td>≤2</td>
<td>≥2250</td>
</tr>
</tbody>
</table>

aReference [7]  
bReference [8]  
cReference [23] 
dReference [9]

pnonential increase. To investigate the sensitivity to pumping area both the lasing properties and far field intensities, from a laser structure with a film thickness of 150 nm, are examined.

Figure 6.8(a) tracks the variation in the threshold as the pump spot radius is decreased from 32 to 8 µm and highlights the rapid increase in threshold fluence for pump radii less than 15 µm. One likely explanation for this trend is that additional losses are incurred in the resonator due to re-absorption in un-pumped regions. In Figure 6.8(b) the lasing input-output characteristics and spectral emission are displayed for the case where the pump spot radius was 18 µm. The inset shows the spectral output collected within a small angle (± 5°) normal to the surface plane of the laser structure. The spectrum was taken with the laser pumped slightly above threshold (at 1.5× threshold) and shows a FWHM of 0.2 nm (instrument limited) that corresponds to a $Q$ factor $\geq 2250$. The characteristics shown in Figure 6.8(b) compare favourably with those previously reported for polymer CBR laser structures (Table 6.1).
Figure 6.8: BN-PFO CBR lasing characteristics: (Top) Laser threshold fluence dependence on pump spot radius $w$. The measured structure is lasing at 450 nm. (Bottom) Laser input-output characteristics and emission spectrum (inset) with a pump spot radius of 18 $\mu$m. The inset data are collected within a small angle ($\pm 5^\circ$) normal to the surface plane of the laser structure. The BN-PFO film thickness is $\sim 150$ nm.

6.5 Modal Properties of the Output Beam

6.5.1 Effect of Excitation Location on Output Beam

The circular nature of the resonator feedback is further revealed by changes in the far-field emission intensity under lasing conditions as the spatial location of the pump spot is translated across the grating field. Spatially-resolved emission intensities are recorded above the surface of the CBR using a high-resolution beam profiler as described before. The polymer laser has a BN-PFO thickness of 105 nm, a grating period of 280 nm, and a duty cycle of
75%. Figure 6.9 shows the results: The pump beam is initially placed at the outer region of the grating and moved inwards towards the centre (see bottom right schematic). When the pump is incident on an outer region of the grating the emitted beam has a double-lobed arc-shape which is confined only in one direction (1). As the pump beam is moved towards the centre, a superposition of several arcs arises, forming a fan-shaped output profile with a hole in its centre, (2) - (4). Image (5) shows the far-field pattern of the output beam when the CBR grating is pumped directly within the central region: A two-dimensionally confined, well-defined circular mode profile with a clear node at its centre and azimuthal polarisation is observed, in close agreement with expectations [13]. The half angle divergence of the output beam is measured to be 5.5 ± 0.5 mrad. In order to understand the formation of this transverse mode profile one has to consider that a guided TE mode which oscillates in a circularly symmetric way must be azimuthally polarised [13]. Thus, the field at any two points on opposite sides of the circle with the same radius $\rho$ will have the same azimuthal polarisation but point in opposite directions. Erdogan and Hall showed theoretically that the electric field must be zero in the centre of the grating [13]. Image (5) does indeed show a clear node of small diameter compared to the overall output beam.

To confirm the azimuthal nature, when the laser beam is passed through a polariser the light intensity should have a flatline behaviour as a function of angle. A series of spectra above threshold are acquired for various rotation angles of the polarisation axis, both for the CBR laser as well as a conventional 1D DFB laser. By plotting the integrated emission intensity within a narrow spectral band centred on each of the laser peaks as a function of the polarisation angle it is possible to demonstrate the differences in polarisation. Figure 6.10 shows the normalised output intensity as a function of the polariser angle for the CBR laser when pumped directly in the centre (red) and for a conventional linear 1D grating (black).

The emission from the CBR laser is relatively unpolarised. The egg-shaped
Figure 6.9: Images recorded from a beam profiler positioned above the surface of the CBR resonator. Image (1) is recorded when the grating is pumped in the outer region. Images (2) to (4) are recorded as the pump spot is moved towards the centre and image (5) is recorded when the pump beam is centred on the grating centre. The pump spot radius is 50 µm and for each image the pump spot is moved 20 µm towards the centre. The pump energy is 3× larger than the threshold energy for lasing.

deformity of the polarisation characteristics and the offset between the start and end of the curve at 0° are due to a drift in the pump intensity during the acquisition of the data. The strong polarisation of 28:1 in the case of the conventional 1D DFB laser (black curve) indicates linear polarisation in clear contrast to the weakly polarised emission from the CBR laser which has a polarisation ratio at best of 1.4:1.

The higher confinement of the emission beam for central pumping is an indication of an improved $Q$ factor for the resonator. Figure 6.11 shows
the FWHM linewidths $\Delta \lambda_{\text{laser}}$ corresponding to the CBR lasing modes presented in Figure 6.9. They lie in the range 0.17 (instrument limited) to 0.3 nm, with longer linewidths occurring for pumping in the outer region of the grating. This data leads to $Q$ factors between 1486 and 2622. Thus, the $Q$ factor can be altered by $\pm 27\%$ simply by translating the pump spot. Given typical linewidths for standard commercial edge emitting Fabry-Perot semiconductor lasers of order $\Delta \lambda_{\text{laser}} \sim 1 \text{ pm}$ [24], the question arises as to what factors contribute to the broad observed linewidth for polymer lasers based on circular resonators. First, all such gratings are based on second-order Bragg diffraction. Such an approach induces efficient vertical emission from the device but decreases the overall $Q$ factor due to higher outcoupling losses. Another possible explanation might be that the polymer films, when deposited on the resonators, fail to fill the grating grooves and hence cause non-ideal feedback. Although it has been reported that the duty cycle has a very strong influence on the polymer-air surface modulation [9], to the author’s knowledge, there has been no detailed investigation of the
Figure 6.11: (Blue) FWHM of the emitted laser modes as a function of the pump centre location on the CBR structure, and (red) corresponding $Q$ factors. Excitation position '0' represents centred pumping of the circular resonator.

substrate-polymer interface yet.

6.5.2 Effect of Excitation Intensity on Output Beam

Emission spectra of a CBR laser for different pump pulse fluences are displayed in Figure 6.12. The spectra are measured without a polariser in the detection path. As can be seen in Figure 6.13, the threshold fluence is $33 \mu J/cm^2/pulse$ (652 pJ, $r_{pump} = 25 \mu m$, $\tau_{pulse} \sim 23$ ns). The data shows that the linewidth is essentially stable for pump pulse fluences up to three times threshold, $3 \times F_{thr}$. There is then an abrupt doubling of the FWHM associated with the appearance of a second mode at $\lambda_{laser} = 440.2$ nm for increasing exitation intensities. This behaviour demonstrates the onset of double mode lasing above three times threshold. The FWHM, $\Delta \lambda_{laser}$, of this laser line versus pump pulse fluence, $F$, is displayed in Figure 6.13(c). The laser linewidth around laser threshold is $\Delta \lambda_{laser} = 0.21$ nm. Just above three times threshold, it jumps to $\sim 0.4$ nm and broadens to $\Delta \lambda_{laser} = 0.5$ nm at high excitation fluences.
Figure 6.12: CBR-laser spectral distribution for several pump laser fluences, $F$. (a) $F = 2.2 \times F_{\text{thr}}$, $\lambda_{\text{laser}}^{\text{max}} = 440.4$ nm, (b) $F = 3 \times F_{\text{thr}}$, $\lambda_{\text{laser}}^{\text{max}} = 440.4$ nm, (c) $F = 5.9 \times F_{\text{thr}}$, $\lambda_{\text{laser}}^{\text{max}} = 440.2$ nm, (e) $F = 11 \times F_{\text{thr}}$, $\lambda_{\text{laser}}^{\text{max}} = 440.2$ nm, (d) $F = 14.8 \times F_{\text{thr}}$, $\lambda_{\text{laser}}^{\text{max}} = 440.4$ nm.

The peak wavelength, $\lambda_{\text{laser}}$, also remains independent of the pump pulse fluence for moderate excitation intensities but starts to alternate between 440.4 nm and 440.2 nm for pump intensities above $4.5 \times$ threshold as can be seen in Figure 6.12 and as is explicitly shown in Figure 6.13(b). The laser output intensity as a function of input pump pulse fluence is shown in Figure 6.13(a). As for both laser linewidth and peak wavelength, the output intensity shows a non-linear dependence on increasing pump intensity. While its slope seems to be constant for moderate pump fluences, a slope change around $3 \times F_{\text{thr}}$ indicates additional emission from a second lasing mode. At high excitation fluences however, the CBR laser output saturates. This saturation behaviour is thought to be due to the fact that light travelling through the waveguide is so strong that it depletes a significant fraction of the excitons [4], or due to exciton-exciton annihilation processes at high
Figure 6.13: (a) Output intensity, (b) peak wavelength and (c) FWHM of laser emission as a function of threshold fluence when the CBR laser is pumped at the centre. For pump fluences below $2.5 \times$ threshold, the emission is single mode with a very narrow linewidth of $\sim 0.21$ nm. Above $3 \times$ threshold, it suddenly becomes multi mode lasing with an increasing linewidth and a change of slope. (b) shows that the peak emission alternates between two wavelengths.

densities of excited repeat units [25].

The polarisation characteristics of the various lasing modes shown in Figures 6.13 and 6.12 are investigated by introducing a linear polariser into the emission collection path, between the CBR laser and the optical fiber in Figure 6.4. The pump pulse fluence is increased from threshold, at $33 \mu J/cm^2$, to about $16 \times$ threshold, such that modes belonging to both regimes discussed above can be observed. A series of spectra are obtained for various rotation angles of the polarisation axis. Plotting the integrated output intensity within a narrow spectral band encompassing each individual lasing peak against the polarisation angle, the two different polarisation characteristics
become clear. Figure 6.14 plots four polarisation characteristics which are representative of the modes in each regime. The emission from the modes of the first regime, at moderate excitation intensities, is relatively unpolarised, as shown in Figure 6.14(a). The deformity of the polarisation characteristics and the offset between the start and end of the curve near $0^\circ$ are partly due to fluctuations of the intensity of the pump laser beam. Thus, polarisation ratios were low with (black curve) $1.6:1$ for pumping at $1.6 \times F_{\text{thr}}$, and $1.4:1$ for pumping at $3.2 \times F_{\text{thr}}$. On the other hand, Figure 6.14(b) shows that the emission from the modes of the second regime, at high excitation intensities, is partially polarised, indicating a strong influence of linearly polarised modes. Here, polarisation is $8.2:1$ at $6.3 \times F_{\text{thr}}$, and $6:1$ at $15.9 \times F_{\text{thr}}$.

Circularly shaped laser beams have been observed in polymer lasers before [5, 7, 26]. However, it has been shown in 2D linear DFB resonators that these circular or 'doughnut' shape beams evolve into a cross-shaped output profile for high excitation energies [26]. On the other hand, Jordan et al. have reported for inorganic lasers that this circular beam only occurred for a certain input power and vanished for powers away from that operation point [27]. The question remains as to what causes this sensitivity of the polarisation state of the emission. It is known that slight deviations from the ideal circularly symmetric resonator structure, for instance due to stitching errors in the e-beam lithography process, cause a departure from the expected modal field. A slight ellipticity, for example, could lead to enhanced outcoupling of light linearly polarised along the longer axis of the distorted resonator [28, 29]. On the other hand, the fabrication process of the CBR structures used here was chosen in order to avoid stitching errors that break radial symmetry.
Figure 6.14: Integrated output intensity versus polariser angle for CBR laser modes for increasing pump pulse fluences. (a) Laser modes of the moderate pumping regime, (black curve) $1.6 \times F_{\text{thr}}$ and (red curve) $3.2 \times F_{\text{thr}}$, exhibit approximately unpolarised emission. (b) Laser modes of the high excitation regime, (black curve) $6.3 \times F_{\text{thr}}$ and (red curve) $15.9 \times F_{\text{thr}}$, exhibit partially polarised emission.

6.6 Summary

This chapter presented the results of a systematic study into optically pumped blue-emitting polymer lasers that are based on circular Bragg resonators. An optimised design strategy was implemented and involved matching the grating profiles with the nulls and maxima from the Bessel functions that represent the radial distribution of the field in a circular resonator.

From a series of designs, lasing operation was demonstrated over a large
spectral range, i.e. $\Delta \lambda \sim 27$ nm around 450 nm, and the threshold energies required were found to be less than 30 $\mu$J/cm$^2$ with the lowest thresholds (1.2 $\mu$J/cm$^2$) obtained when the lasing oscillation was coincident with the peak wavelength of the ASE gain spectrum.

An influence of the pump location on the laser linewidth and hence the $Q$ factor was observed. For central pumping of the CBR resonator, a single lasing mode was seen in the spectrum and indicated a $Q$ factor of at least 2620 (although this value was limited by instrumental resolution). The circular nature of the resonators was investigated by monitoring the output beam profiles under various pumping configurations. Exciting the structures directly in the centre of the gratings revealed a clear circular mode, with azimuthal polarisation character and a half-angle beam divergence of 5.5 mrad.

The impact of the pump intensity on the emitted modes was systematically studied. The results show that these CBR devices are able to operate as single mode lasers with azimuthal polarisation for moderate excitation intensities up to more than $3 \times F_{\text{thr}}$. Above that a second mode appears leading to a sudden increase of the laser linewidth and the development of a component of linearly polarised emission.

To the best of the author’s knowledge these results represent the shortest wavelength CBR-based lasers reported to date and are testament to the high quality fabrication techniques that are available with contemporary E-beam lithography.
Bibliography


Chapter 7

Conclusions

7.1 Thesis Summary

Following the encouraging successes of organic semiconductor materials in
the commercialisation of displays, thin-film transistors, solar cells and light-
ing applications, a lot of attention is currently focusing on the development
of small molecule and especially polymer lasers. Conjugated polymer lasers
are a fascinating class of laser devices with the potential to offer low priced
solutions for sensing applications. The ease of fabrication and the ability
to cover the entire visible and NUV spectral region are only two of their
advantageous properties which are complemented by the fact that polymers
can be deposited as thin films even on flexible substrates, using inexpensive,
simple, large-area, low temperature, high-throughput techniques.

This thesis reported a study on the design and characterisation of optically
pumped blue and violet emitting polymer lasers. The laser devices were
based on a range of materials belonging to the polyfluorene family of con-
jugated polymers which generally show efficient, low threshold stimulated
emission. For future electrically pumped polymer lasers, a further reduction
of the threshold is crucial since a low threshold fluence directly translates
into low current densities.

The optical properties of in total three polyfluorene polymers were investi-
gated. These are the violet light emitting poly(9,9-dioctylfluorene-co-(2,5-dioctyloxy)-p-phenylene) (FOP), and two blue light emitting copolymers. One is based on 2,7-(9,9-dioctylfluorene) repeat units with a minor portion of statistically incorporated 6,6-(2,2-octyloxy-1,1-binaphthyl) groups (BN-PFO) and the other statistical copolymer is made up of 80% 9,9-dioctylfluorene and 20% 9,9-di(2-methyl)butyl fluorene monomer units (Y80F8:20F5).

Lasers based on the copolymer FOP were optically-pumped and emission wavelength tuning was demonstrated by altering both grating period and gain polymer thickness, allowing us to cover a part a spectral region between the blue and ultra-violet that has not been addressed yet by organic semiconductor lasers (418.9 to 447.1 nm). Lasers based on a shorter period grating were found to have a weaker sensitivity to changes of the gain polymer thickness which might prove to be a beneficial feature for sensing applications.

Furthermore, a systematic numerical study of the optical environment on the performance of blue emitting lasers on conducting DFB resonators was presented, which was followed by a demonstration of optically pumped polymer lasers based on ITO gratings. Findings from both simulations and experiments suggest that in order to overcome limiting factors set by the presence of electrode materials, a combination of high refractive index gain polymers and low refractive (conducting) inter-layers is desirable. In particular, one conclusion from the conducted work in this thesis is that a high refractive index for the gain polymer helps to mitigate absorption losses due to an ITO contact and to enable the overall device thickness to be kept to realistic dimensions.

Finally, the results of a systematic study into optically pumped blue emitting polymer lasers based on circular Bragg (CBR) resonators were reported. An optimised design strategy was implemented and involved matching the grating profiles with the nulls and maxima from the Bessel functions that
represent the radial distribution of the field in a circular resonator. From a series of designs, lasing operation was demonstrated over a large spectral range, i.e. $\Delta \lambda \sim 27$ nm, and threshold fluences as low as $1.2 \mu J/cm^2$ were attained. For central pumping of the CBR resonator, a single lasing mode was seen in the spectrum and indicated a $Q$ factor of at least 2620. The circular nature of the resonators was investigated by monitoring the output beam profiles under various pumping configurations. Exciting the structures directly in the centre of the gratings revealed a clear circular mode with azimuthal polarisation character. The impact of the pump intensity on the emitted modes was systematically studied. The results show that these CBR devices are able to operate as single mode lasers with azimuthal polarisation for moderate excitation intensities up to more than $3 \times F_{\text{thr}}$. Above that a second mode appears leading to a sudden increase of the laser linewidth and the development of a component of linearly polarised emission.

For a comprehensive summary of the results obtained from the studies in this thesis the reader is referred to the individual summary sections at the end of each chapter.

### 7.2 Suggestions for Future Work

In order to make progress on the way towards a polymer laser diode it is important to recognise the major challenges for research and development. Amongst the identified issues that lead to problems with structures that are suitable for electrical pumping are the optical losses due to absorption in the electrode materials. One solution to this issue is a multi-layer concept that combines a high refractive index gain layer with low refractive index inter-layers. This would enhance the optical confinement in the gain polymer and reduce the mode penetration into absorptive electrode materials. An introductory discussion on this has been given in Chapter 5. Additionally, a high index polymer would also enable the reduction of the overall film thickness of a potential laser diode as compared to lower index gain polymers.
This would allow for higher current densities to pass through the polymer laser device.

The development of transparent electrodes might also prove to be very promising. An attractive, highly conducting material is the vapour-phase polymerised poly (3,4-ethylenedioxy) thiophene (VPP PEDOT) which has been applied in a variety of device types including photodiodes, OLEDs and photovoltaic cells [1–3]. Furthermore, the refractive index of VPP PEDOT layers is expected to be significantly lower than ITO [4], which would lead to stronger mode confinement in the gain polymer layer.

Apart from these ideas, the concept of lasers based on organic field-effect transistors (OFET) has been attracting a lot of attention [5–9]. However, to date, the current densities that can be realised in organic thin film transistors are still about an order of magnitude too low [5, 10, 11].

Progress towards electrically pumped polymer lasers will require polymer materials with increased charge carrier mobilities. So far, the understanding was that this will not only allow thicker films and hence reduce the mode confinement in the electrodes but also reduce losses through polaron absorption. However, Karnutsch in simulations has shown that unless the mobilities of the gain polymer as well as the inter-layers are increased simultaneously, the effect of polaron absorption will not be reduced [12].

An alternative to a polymer laser diode could be a hybrid organic-inorganic solution that uses an inorganic light-emitting diode to pump an organic gain material. Yang et al. have recently reported such a structure [13]. These hybrid laser architectures could provide the basis for extremely low-cost portable lab-on-a-chip analysis devices emitting across the near ultra-violet and visible spectral region. A concept employing inorganic µLEDs with 70 µm diameter is currently being evaluated in our group.

As soon as organic laser diodes are ultimately realised they have great potential in a large number of fields, offering very versatile and cheap laser sources. Their large spectral tuning range opens possibilities for laser-based
sensing techniques. Furthermore the inherent mechanical flexibility together with the possibility of large-area fabrication might offer novel solutions for mechanical scanning procedures. In conclusion, organic semiconductors and especially conjugated polymers are an exciting playground for the exploration of innovative laser concepts and devices.
Bibliography


8.1 Wave Equation

Assuming that there are no free charges ($\rho = 0$) and no current ($J = 0$), the required Maxwell equations can be written as

\[
\nabla \times \mathbf{E} + \frac{\partial \mathbf{B}}{\partial t} = 0, \tag{8.1}
\]

\[
\nabla \times \mathbf{H} - \frac{\partial \mathbf{D}}{\partial t} = 0, \tag{8.2}
\]

\[
\nabla \cdot \mathbf{D} = 0, \tag{8.3}
\]

In the absence of any magnetic or dielectric materials, the relationships between $\mathbf{D}$ and $\mathbf{E}$ as well as that of $\mathbf{B}$ and $\mathbf{H}$ are given by

\[
\mathbf{D} = \varepsilon \mathbf{E}, \tag{8.4}
\]

\[
\mathbf{B} = \mu \mathbf{H}. \tag{8.5}
\]

Using equation (8.5), equation (8.2) becomes

\[
\nabla \times \left( \frac{1}{\mu} \mathbf{B} - \frac{\partial \mathbf{D}}{\partial t} \right) = 0. \tag{8.6}
\]

With equation (8.4) in (8.6), we can write

\[
\nabla \times \mathbf{B} - \mu \varepsilon \frac{\partial \mathbf{E}}{\partial t} = 0. \tag{8.7}
\]
Taking the curl of equation (8.1)
\[ \nabla \times \nabla \times E + \frac{\partial}{\partial t} (\nabla \times B) = 0, \] (8.8)
and then using equation (8.7), we can write
\[ \nabla \times \nabla \times E + \mu \varepsilon \frac{\partial^2 E}{\partial t^2} = 0. \] (8.9)

By using the vector identity
\[ \nabla \times (\nabla \times E) = \nabla (\nabla \cdot E) - \nabla^2 E \] (8.10)
equation (8.9) can be written as
\[ \nabla (\nabla \cdot E) - \nabla^2 E + \mu \varepsilon \frac{\partial^2 E}{\partial t^2} = 0. \] (8.11)

Finally, by considering equations (8.4) and (8.3), equation (8.11) turns into the wave equation
\[ \nabla^2 E - \mu \varepsilon \frac{\partial^2 E}{\partial t^2} = 0. \] (8.12)

This is the wave equation for the electric field vector, \( E \), in homogeneous and isotropic media. Accordingly, the magnetic field vector, \( H \), can be written
\[ \nabla^2 H - \mu \varepsilon \frac{\partial^2 H}{\partial t^2} = 0. \] (8.13)
8.2 Simulation Parameters

Employed parameters for the simulations in Section 5.3.

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