HÁSKÓLI ÍSLANDS

Fluorescent polymers as integrated light sources

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Contents

Abstract

In this study we discuss the use of fluorescent polymers in
dielectric waveguides. Fluorescent polymers have developed rapidly
in recent years, with direct applications to optical biosensing.
Fluorescent polymers can induce an optical gain, enabling fabrication
of optically pumped amplification and laser-sources. We discuss and
demonstrate the fabrication of planar waveguides, where a symmetric
waveguide supporting a single guided mode was desired, which can
then be directly integrated with microfluidic circuits that have
previously been studied by the group.

1 Introduction

Integrated optical technology has become increasingly popular, with wide-
spread applications in the telecommunication industry and biological sci-
ences. Recently, fluoropolymer-based optical devices have been introduced
by researchers at the University of Iceland, for various sensing and monitor-
ing applications, e.g., for live cell-biology [1][2], where they can be directly
integrated with conventional PDMS microfluidic components to form com-
plex lab-on-chip devices [3][4]. Furthermore, polymer based waveguides have
interesting optical and chemical properties that are suitable for biosensing
applications, while they are also relatively low in fabrication costs. Com-
mercially available optical polymers have a wide range of refractive indices,
ranging from $n \sim 1.3$ to 1.7. The amorphous perfluorinated polymer CY-
TOP, referred to above, has an index of refraction ($n \sim 1.34$) close to that of
water ($n \sim 1.33$), making it possible to highly index-match a CYTOP based
cladding material to an optically probed sample solution [5].

Conjugated fluorescent polymers are among the organic materials that
show maximum optical gain. Such polymers are used, e.g., in the fabrica-
tion of organic light emitting (OLED) devices. According to Xia *et al.* [9],
achievable net gain can be maximized by using a mixture of a large-bandgap
polyfluorene with a small-bandgap polymer as a gain material to reduces self-
absorption losses (self-quenching). Here, we discuss the fabrication of polymer

based channel waveguides with an optically pumped layer of conjugated fluorescent polymer blend adjacent to the channel. We chose to use two polymer variants from American Dye Source (ADS) with a higher-bandgap material used purely as a means of reducing self-absorbtion. Both variants are commonly used in organic electronics, light emitting displays, organic solar cells and in biosensing [8][10][11].

The hybrid polymer Ormoclear, which is commonly used for micro-optical applications, was chosen as the channel waveguide material [13]. It is UV-patternable at room temperature making it suitable for processing by standard lithography and imprinting techniques. We also try using PMMA as a channel material, but PMMA channels can be patterned by e-beam or DUV lithography. Discussions of CYTOP-PMMA devices previously fabricated by the group can be found in [1][2][5].

2   Materials and methods

Here follows a description of the materials used along with fabrication outlines. All fabrication took place in a class 100 cleanroom at the University of Iceland.

2.1   Materials

The two types of flourescent polymer, ADS104RE and ADS133YE, were supplied from American Dye Source, Inc. The fluorescent solution was prepared by dissolving ADS104RE and ADS133YE in a 5:4 mixing ratio in toluene, a frequently used organic solvent.
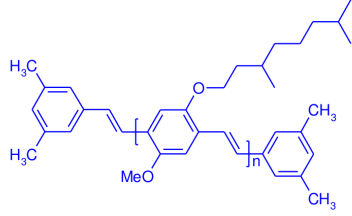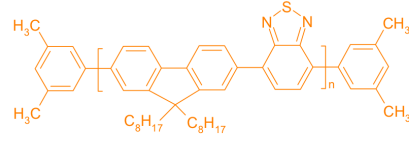
<div align="center">(a) ADS104RE   (b) ADS133YE</div>

Figure 1: Chemical structure of the fluorescent polymers used, images taken from [10] and [11].

The PMMA variant 950PMMA-A, was supplied from MicroChem Corp. Solutions of 2%, dissolved in anisole were used, but according to the datasheet [12] a spin coated solution at 1500 rpm yields a thickess of around 100 nm.

Ormoclear (Micro Resist Technology) is a hybrid polymer and commonly used for micro-optical applications. Two solvents were tested for Ormoclear solutions, maT-1050 and Ormothin. maT-1050 in a 20:1 ratio with Ormoclear was ultimately used for the fabrication of samples, giving a more homogeneous spin coated Ormoclear layer than Ormothin based solutions. Ormoclear layers were developed in Ormodev, a developer for hybrid polymers.

The perfluorinated polymer CYTOP (CTX809AP2 - from Asahi glass company) has many interesting properties, it has an index of refraction ($n \sim 1.34$) close to that of water ($n \sim 1.33$) enabling close index-matching of the cladding material with a sample solution of biological origin. The adhesion promoter AP3000 supplied from Dow Chemical Company was used for surface layer treatments before CYTOP coating in order to promote better surface adhesion. Al layers (for CYTOP surface treatment) were removed in ma-D331 alkaline solution.

Other materials included N_2 gas used both for purging and blow drying, IPA (Iso-propyl alcohol), acetone and methanol; mainly used for cleaning purposes. All silicon wafers (100 mm) were supplied from Silicon Quest International.

2.2 Methods

2.2.1 Thickness experiments

Several Ormoclear and ADS-layer thickness experiments were performed to characterize the effect of spin speed and mixing ratios. We varied the amount of solvent used to dissolve Ormoclear, trying both Ormothin and maT-1050. Layer thicknesses were measured using an ellipsometer. 1-dimensional mode-solver calculations (see Figures 6, 7 and 8) revealed that an Ormoclear thickness of 100 nm along with a comparable size in the fluorescent layer thickness supported a single (transverse) guided mode.

Furthermore, we had to address whether toluene, the solvent used for the fluorescent polymers, had any chemical effect on Ormoclear, e.g., serving to reduce Ormoclear thicknesses or deteriorate its optical properties. These effects were evaluated by measuring Ormoclear thicknesses and refractive index before and after soaking Ormoclear layers in pure (>99.5%) toluene.

2.2.2 Waveguide fabrication

Figures 2 and 3 show the processing steps needed to fabricate 2-dimensional waveguides with and without an Ormoclear layer.

First, a 100-mm Si wafer [100] is baked at 200° on a hotplate for 5 minutes, to remove adsorbed moisture. Then a thin layer of adhesion promoter (AP3000) is applied before spin coating CYTOP at 3000rpm for 30s. The wafer is subsequently heated in an oven from 50° to 180° in 30 min, baked for 1 hour and then cooled down to room temperature. A thin layer of Al is deposited by a thermal evaporation device (cryofox), to make the CYTOP surface hydrophilic, before dice cutting into smaller
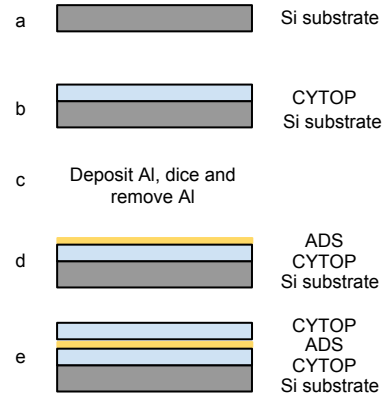

Figure 2: Processing steps for a polymer slab waveguide: (a) A clean Si wafer; (b) CYTOP is spin-coated on Si wafer; (c) Al is deposited, wafer diced to smaller samples, Al removed; (d) A fluorescent polymer solution is applied; (e) CYTOP spin coated, forming a complete device.

(2cm×2cm) samples. The Al was subsequently removed using a maD-331 photoresist developer (NaOH solution).

As is illustrated in steps IV-VI in figure 3, both placing the fluorescent layer over and under the waveguide layer was tried. Fluorescent polymer was deposited by spin coating at 1000rpm and 2000rpm, while Ormoclear was spun at faster rates (2000rpm and 4000rpm) to achieve similar thickness to ADS.
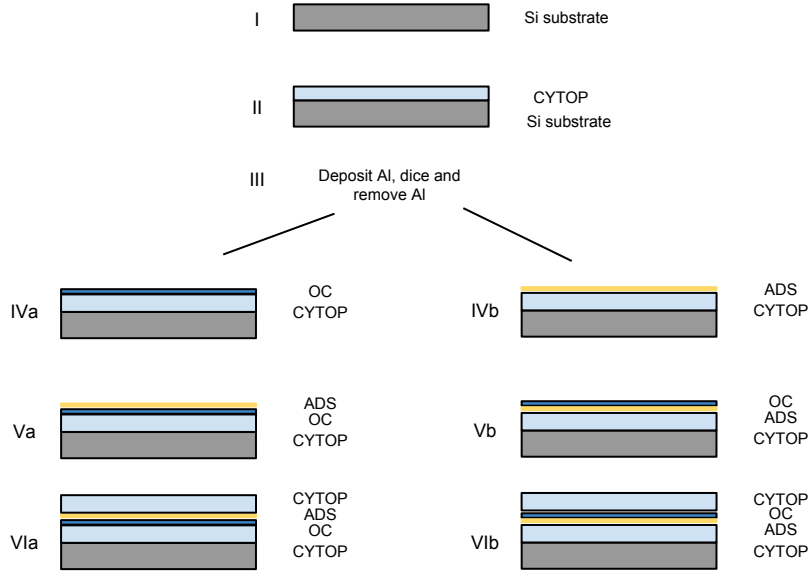

Figure 3: Processing steps for slab waveguides with an Ormoclear layer. The first three steps are the same as outlined in Figure 2. The left side illustrates a waveguide fabricated with a fluorescent gain layer on top of the Ormoclear layer, while the right side shows the same waveguide with the fluorescent layer below the Ormoclear core waveguide material. Channels can be defined in Ormoclear by UV-exposing under a mask (see Figure 4).

2.3 Channel waveguides

Channel waveguides were introduced in Ormoclear by standard UV-lithography techniques using a mask defining (nominally) 2–12μm-wide channels. Channels can also be patterned directly in PMMA by deep-UV lithography or by

direct e-beam lithography (if coated by a thin layer of Al to prevent charging). Figure 4 outlines the steps needed to fabricate channel waveguides.
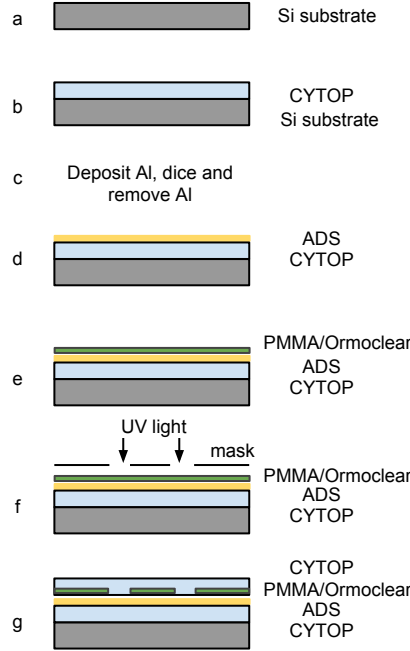

Figure 4: Steps outlining the fabrication process of a channel waveguide with a patternable PMMA or Ormoclear core waveguide layer. (a) A clean Si wafer; (b) CYTOP spin coated on Si wafer; (c) Al is deposited, wafer diced to smaller samples, Al removed; (d) Fluorescent polymer solution applied by spin coating; (e) PMMA/Ormoclear layer spin coated; (f) Channels defined by lithography; (g) Top CYTOP cladding layer applied, to form a complete device.

3 Results and discussion

3.1 Polymer thickness

Layer thicknesses were measured using an ellipsometer. Successively thinner solutions of Ormoclear dissolved in maT-1050 were tried. A mixing ratio of 1:20 of Ormoclear in MaT-1050 spun at 2000-4000rpm was found to give a homogeneous Ormoclear layer.

3.2 Effects of toluene on Ormoclear

Thickness of Ormoclear layers was measured before and after a soaking treatment for 30 s and 150 s in pure (>95%) toluene. Little to no effect on Ormoclear thicknesses was measured, but according to but according to [13], Ormoclear has a high chemical and physical stability.

3.3 Mode calculations and sample fabrication

Figures 6, 7 and 8 illustrate seven of our fabricated waveguide geometries, along with their measured layer thicknesses and calculated mode profiles. Slight polymer delamination was observed after dicing some of our fabricated samples, as shown in Figure 5a, potentially increasing waveguide scattering. Furthermore, debris particles due to dicing could also stick to the top waveguide sample layer, further increasing scattering. This effect could be reduced by constantly spraying the sample with water during dicing.

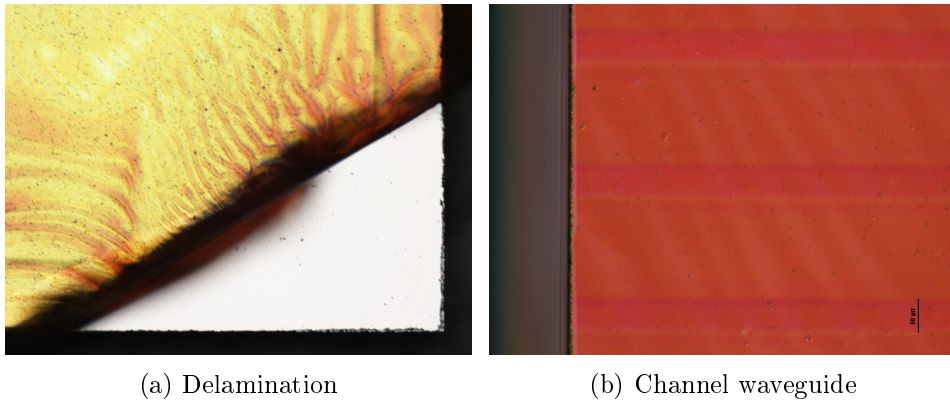|(a) Delamination | (b) Channel waveguide |

Figure 5: (a) Delamination at the edge of a waveguide sample after dicing; (b) A complete Ormoclear channel waveguide, where the black line indicates $50\mu m$. Some scattering particles due to the dicing process can be seen.

The emission spectra for the samples are shown in Figure 10. The mode profiles were modeled using the experimentally measured thicknesses and by using an estimated refractive index for each material. Mode profiles were not measured separately, as the small variations expected from modelling cannot be detected with conventional far-field microscopy.
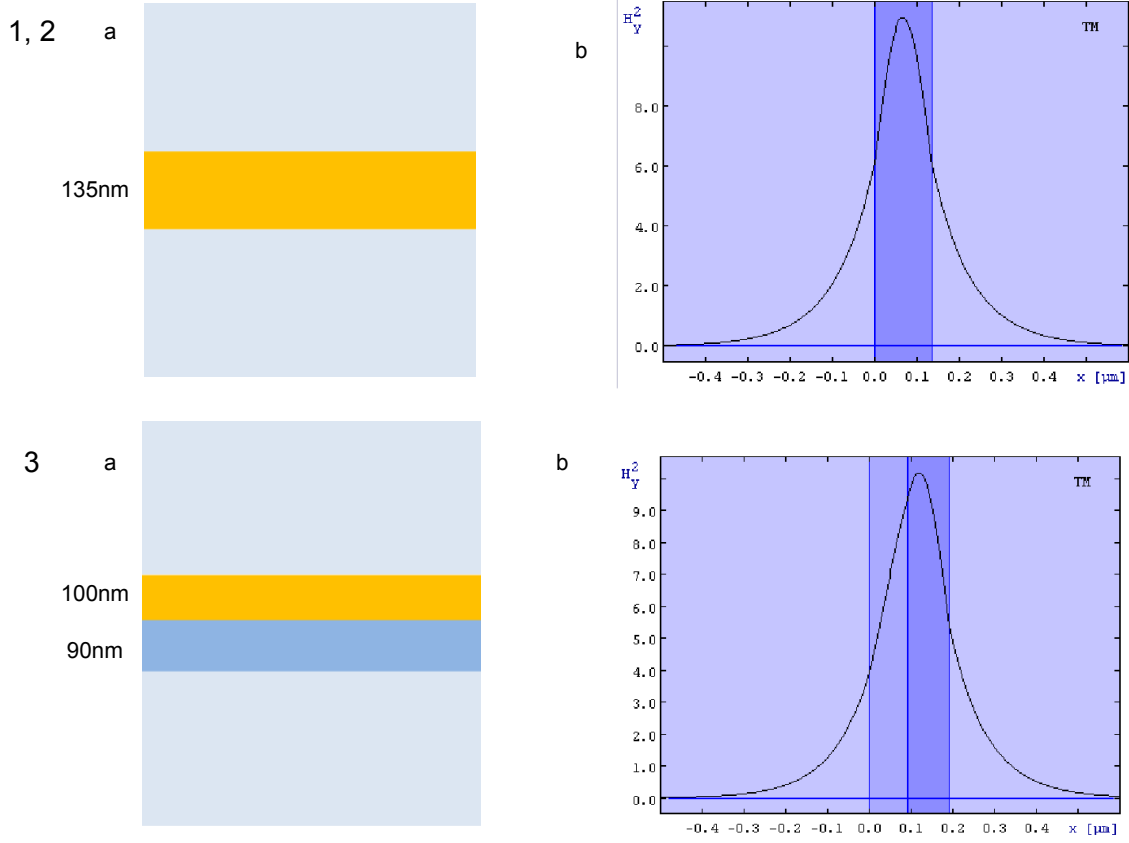
3.3.1 Samples 1,2 and 3

Figure 6: An illustration of samples 1,2 and 3, showing the thickness of respective layers along with calculated mode profiles. Sample 2 is the same as sample 1, but had an extra heat treatment. The waveguides support the single mode.
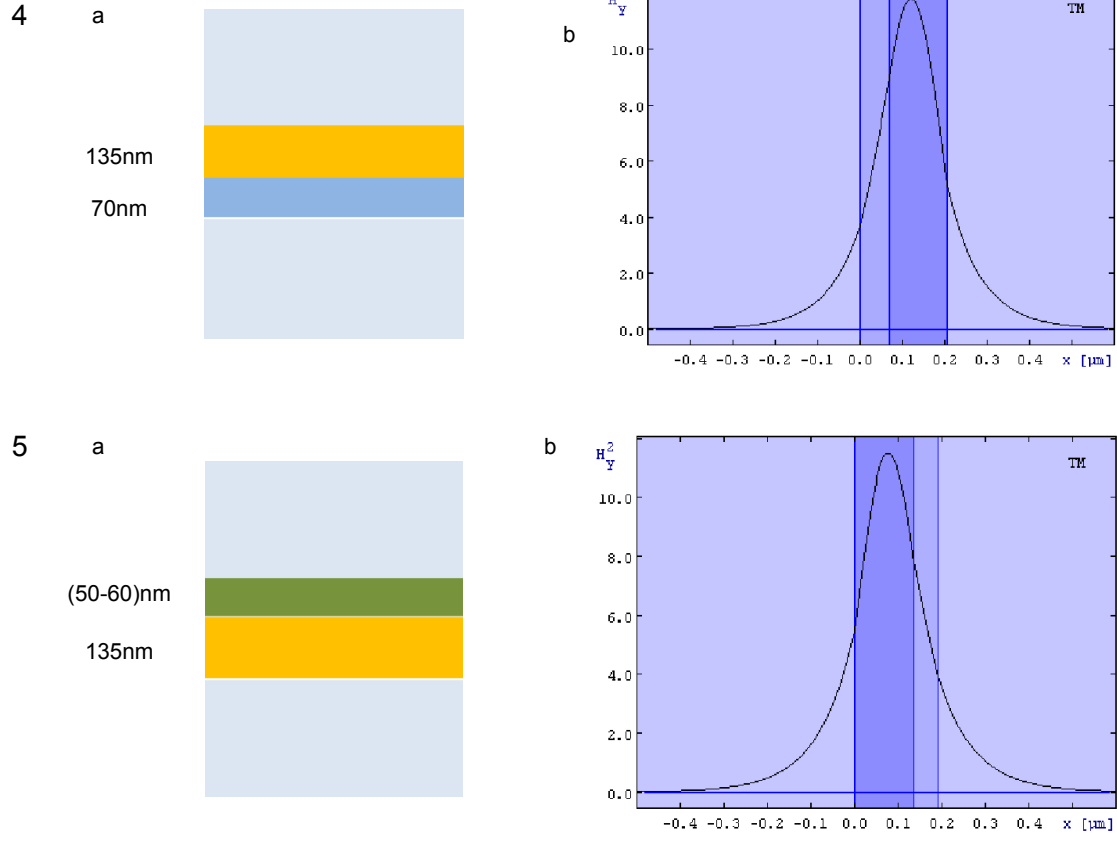
3.3.2 Samples 4 and 5

Figure 7: An illustration of samples 4 and 5 showing the thickness of respective layers along with calculated mode profiles. All waveguides support a single transverse mode.
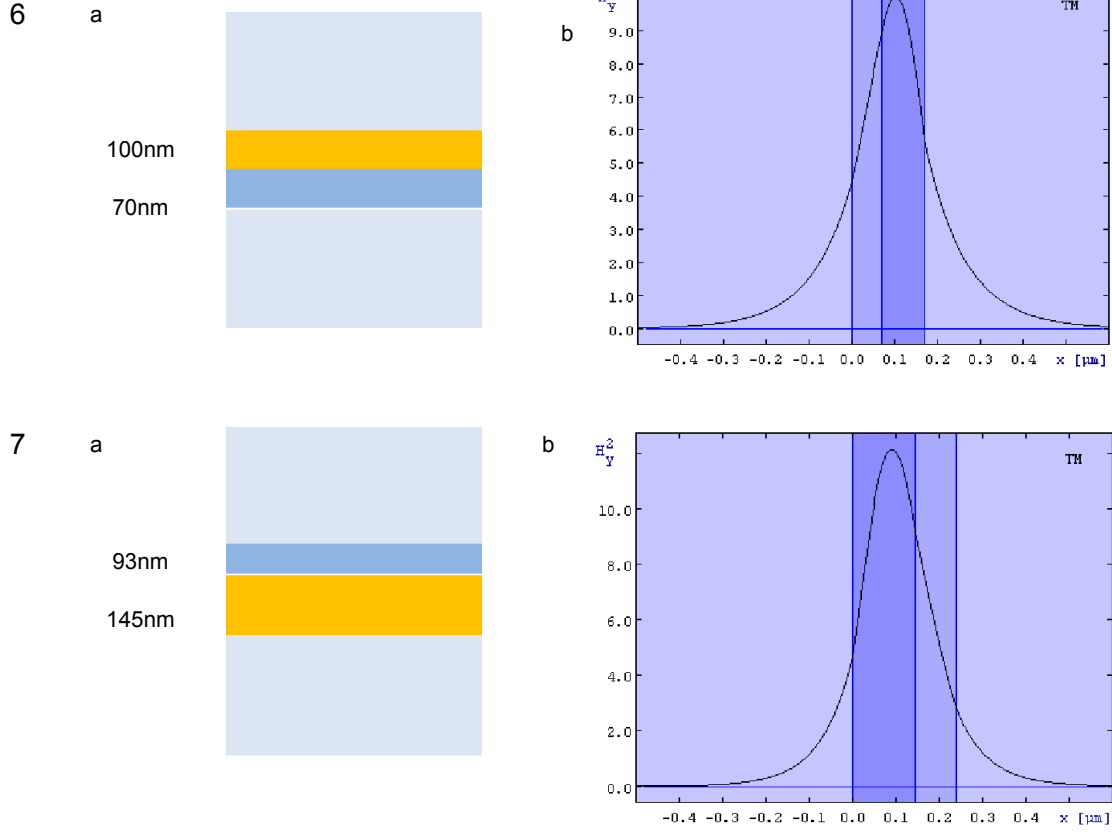
3.3.3 Samples 6 and 7

Figure 8: An illustration of samples 6 and 7, with Ormoclear on top or below the fluorescent layer. The illustration shows the thickness of the respective layers along with calculated mode profiles. The waveguides support a single mode.

3.4 Gain and light propagation

Figure 9 shows the setup for the light emission measurement where a monochromatic laser light with a wavelength of $\lambda = 532\,\text{nm}$ was used as the excitation source. The measured edge and surface emission spectra (at $45°$ emission angle from the normal) are shown in Figure 10. Although a large variance in fluorescence emission is observed between samples, their total emission is comparable. Sample 7, with the Ormoclear layer conveniently on top of the ADS layer, had the highest measured total emission.
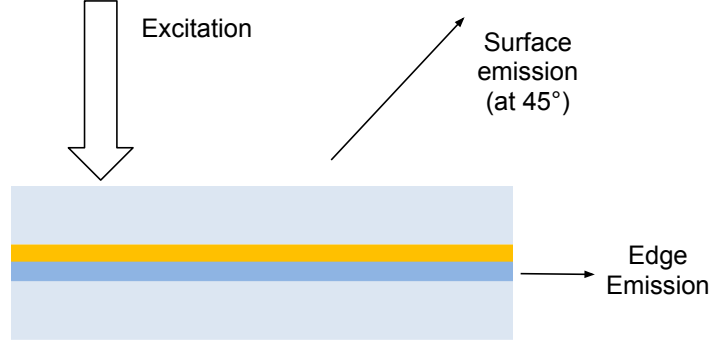
Figure 9: Fluorescence emission measurement setup. Monochromatic laser light with a wavelength of $\lambda = 532\,\text{nm}$ is used as an excitation source. Surface emission (at 45° to the normal) and edge emission spectra are shown in Figure 10

(a) Edge emission
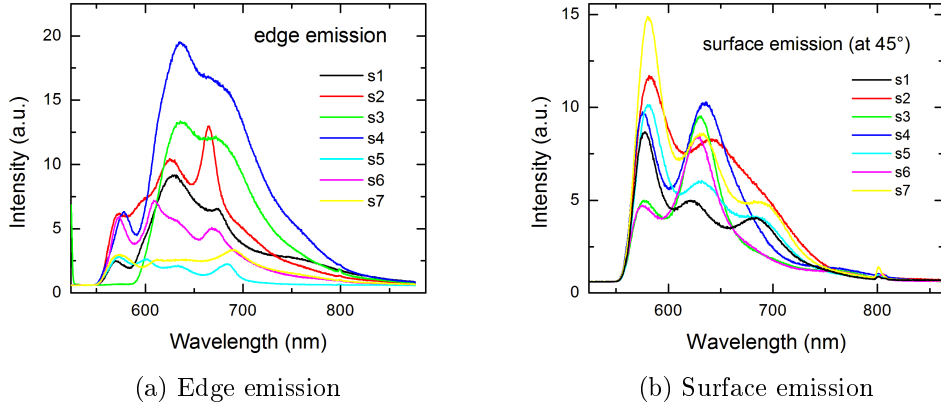

(b) Surface emission

Figure 10: Emission spectra at an excitation wavelength of $\lambda = 532\,\text{nm}$ for the seven samples shown in Figures 6, 7 and 8. Although we observe a large variance in fluorescence between samples, their total emissions are similar.

4   Conclusions

We discuss the fabrication and characterization of polymer waveguides with a fluorescent polymer gain layer where strong fluorescence was observed. However, a significant amount of emitted light is lost through scattering and absorption, potentially reducing the achievable optical gain. Improvement in Ormoclear patterning is required for better defining the channel waveguides,

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but the photomask can not touch the Ormoclear layer during exposure (to avoid it sticking to the mask), reducing the resolution of the lithographic process. Directly focusing a beam of UV light at the sample and patterning the channels with a "laser writing system" could be a possible solution. Scattering can also be reduced significantly if dicing is kept to a minimum.

Furthermore, PMMA based waveguides can be tested further and patterned by using e-beam lithography enabling features around or below the 1-μm regime. An outline of possible configurations for next generation devices are shown in Figure 11. Such configurations will be addressed in continuing work at the institute.
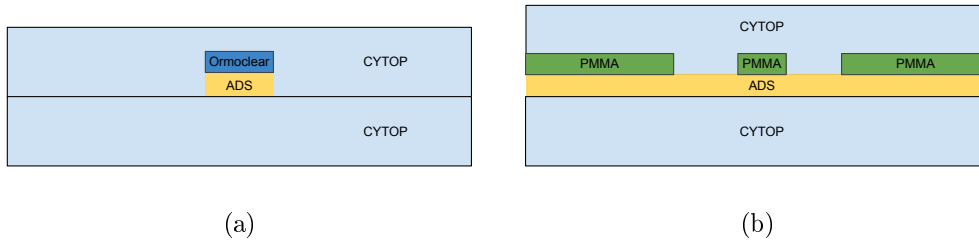

(a)   (b)

Figure 11: Outlines of possible device structures useable as optically pumped light sources.

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