Nanoimprinted Integrated Polymer Optics

Michael Hansen - s991279

Supervisors: Anders Kristensen & Daniel Nilsson

MIC – Department of Micro and Nanotechnology
Technical University of Denmark

August 1, 2005
Abstract

In this thesis, a technology for fabrication of all polymer based Lab-On-a-Chip (LOC) microsystems by Nanoimprint Lithography (NIL) in Topas is presented. The microfluidic channels and optical elements are defined in a layer of Topas grade 8007 by NIL, and sealed with a Pyrex glass lid using an intermediate layer of Topas grade 9506. By using a Topas grade with a lower glass transition temperature, $T_g$, it is possible to fabricate an all polymer device, where the imprinted structures are unharmed by the bonding process. In order to extend the technology to high $T_g$ Topas grades, such as 5013 and 6013, a new anti-sticking coating is introduced. The new coating is based on fluorocarbon chains, that are grafted to a silane head group. The silane head group reacts with the surface of the stamp, thus creating a dense and durable anti-sticking layer, that is covalently bonded to the surface of the stamp.

Two versions of the anti-sticking coating are fabricated and tested. The first is deposited by Molecular Vapor Deposition (MVD) in a commercially available machine, the second is fabricated by Vapor Phase Deposition (VPD) in a machine, that has been designed and constructed for this purpose. Furthermore a process sequence for the fabrication of anti-sticking coatings, in the constructed machine, by VPD is developed. The anti-sticking coatings are tested with respect to durability, and what grades of Topas they are able to imprint into. A comparison is made with the anti-sticking coating previously used for NIL stamps, which was deposited by using the passivation step in a Deep Reactive Ion Etching (DRIE) tool.

Furthermore an integrated LOC is presented. The LOC is demonstrating an approach for integration of an on-chip light source with an optical element, by the use of 2D planar optics. The light source is a microfluidic dye laser, and it is integrated with an absorbance detection cell. The emitted light from the laser is focussed directly into a waveguide by a Fresnel lens. The microfluidic laser is characterized and is emitting laser light between 576 and 590 nm, the lasing threshold is about 70-75 $\mu$J/mm². The functionality of the LOC device is demonstrated by operating the device with different solutions of Xylenol Orange in the absorbance detection cell.

The cutoff conditions for guidance of optical modes in the residual layer is found, and proved experimentally by operating a device with a thick residual layer, and a device without residual layer. It is shown that emitted laser light, in the device with a thick residual layer, escapes the designated light paths, whereas the emitted light is much better guided on the device where the residual layer is removed.

The limitations for the use of Topas is found be several experiments. It will be shown that Topas is able to withstand pumping powers up to 490 $\mu$J/mm² for a pulsed laser beam at 532 nm. Topas’s resistance towards Environmental Stress Cracking (ESC) is tested by
exposing different Topas grades to liquid environments. It is found that high $T_\text{g}$ Topas grades are much more sensitive towards ESC, due to their high $T_\text{g}$. The source for the ESC is identified as the thermal mismatch between the Topas and the silicon substrates.

August 1st, 2005

Michael Hansen, s991279
Dansk Resume

I denne afhandling, vil en teknologi til fremstilling af polymer baserede mikrovæskesystemer (LOC) ved Nanoimprint litografi (NIL) blive præsenteret. Mikrovæskes kanalene og de optiske elementer er defineret i Topas type 8007, og forsøget med et glass lag v.h.a. et mellemliggende lag Topas type 9506. Ved at bruge en type Topas med en lavere glass overgangs temperatur, $T_g$ er det muligt at fremstille en polymer chip, hvor de imprintede strukture ikke tager skade af forseglingsprocessen. For at benytte teknologien i høj $T_g$ Topas typer, som 5013 og 6013, er en ny slags anti-vedhæftnings lag introduceret. Det nye anti-vedhæftnings lag består af kæder af flour og kulstof atomer, der er fastet på en silane gruppe, som reagerer med overfalden på stemplet og danner et tæt og holdbart lag, som er kvalent bundet til stemplet.

To udgaver af denne overfaldebehandling er fremstillet og testet. Den første er fremstillet v.h.a. "Molecular Vapor Deposition" i en kommersiel maskine, den anden er fremstillet ved "Vapor Phase Deposition" (VPD) i en maskine, som er fremstillet til formålet. En processfølge for fremstillingen af anti-vedhæftnings lag ved VPD blevet udviklet. Anti-vedhæftnings lagene er blevet testet med henblik på holdbarhed, og hvilke Topas typer de kan imprime i. En sammenligning med den type anti-vedhæftnings lag, som tidligere er blevet brugt for NIL stempler, og som er blevet deponeret af passiveringsdelen i en Dyb Reaktiv Ion Ætsnings (DRIE) maskine.

En integreret LOC bliver præsenteret. LOC’en demonstrerer en fremgangsmåde for integrationen af en lyskilde med en optisk komponent, ved at bruge 2D Fresnel linser. Lyskilden er mikrovæskes farvestof laser, og den er integreret med en cuvette for absorbans måling. Laserlyset er fokuseret direkte ind i en bolgeleder af en Fresnel linse. Mikrovæskes farvestof laseren udsender laserlyset mellem 576 og 590 nm, og tænkslen for lasing ligger omkring 70-75 μJ/mm². Det er vist at cuvetten til absorptions målinger fungerer, ved at anvende forskellige opløsninger af farvestoffet Xylenol Orange i cuvetten.

Betingelsen for at afskere optiske bolger i residual laget er fundet, og eftervid ekspementielt ved at bruge et mikrovæskesystem med at tykt residual lag, og en uden et residual lag. Det er vist, at det udsendte laserlyset undslipper bolgelederen i det mikrovæskesystem, hvor der er et tykt residual lag, mens lyset er meget bedre samlet i den hvor residual laget er fjernet.

Begrebsningerne i brugen af Topas er også blevet undersøgt, og det vil blive vist at Topas er istand til at modstå laser pulser på op til 490 μJ/mm², for en pulser laser stråle ved 532 nm. Topas’s modstandsdygtighed overfor omgivelser bestemt revnedannelse (ESC) er testet for forskellige flydende omgivelser. Det er vist at høj $T_g$ Topas typer er meget mere modtagelse for ESC, p.g.a. deres høje $T_g$ kilden til ESC er lokaliseret som den termiske forskel mellem Topas og silicium underlaget.
Preface

This thesis is submitted as a partial fulfillment of the requirements for obtaining the Master of Science degree from the Technical University of Denmark (DTU). The project has been conducted at the Department of Micro and Nanotechnology (MIC) in the period from August 2nd 2004 to August 1st 2005. The thesis title is: *Nanoimprinted Integrated Polymer Optics* and the work done during the project corresponds to 50 ETCS points.

The project has resulted in two accepted conference proceedings, and a journal paper. The journal paper has been written together with Ph.D student Brian Bilenberg. The work on the imprinted Lab-on-a-chip device is going to be presented at: Optics and Photonics 2005, San Diego, July 31st - August 4th 2005, and at: The 19th European Conference on Solid-state transducers, Eurosensors XIX, Spain, September 11th-14th 2005. The work on developing the Topas imprint technology was presented at: The forty-ninth International Conference on Electron, Ion and Photon beam technology and Nanofabrication, Orlando, USA, May 31st - June 3rd, 2005 and a journal paper is due to appear in: Journal of Vacuum Science and Technology B in 2005.

I would like to thank my main supervisor Anders Kristen, for his enthusiastic guidance through the entire project. Anders has been a key source of motivation and inspiration, and he has always had the time to listen and discuss new ideas. I would also thank my assistant supervisor Daniel Nilsson for introducing me to the field of Nanoimprint Lithography. I would like to thank the entire Nanoimprint group for creating a fruitful working environment and specially Ph.D. student Søren Balslev for his invaluable support regarding the microfluidic dye laser and the optical setup used in this project.

I would also like to thank Poul Erik hyldbo, Jonas Michael Jensen, Jakob Geert Petersen for help with construction of the anti-sticking chamber, Peter Szabo for help with the viscosity measurements, the cleanroom staff for always being ready to help and provide qualified input regarding cleanroom processing, my friends Anders Greve and Henrik Andersen for proof reading the thesis, and my fellow master students in room 119, for the many hours of unproductive fun that made my stay at MIC such a pleasant one.

I would also thank my friend in Venstres Ungdom for dragging me away from the laboratories once in a while for some fun and amusements.
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Chapter 1

Introduction

In 1990 Manz et al. [1] introduced the concept of miniaturized Total Analysis Systems (μTAS) in their ground breaking paper. The μTAS concept proposes the miniaturization of a full analytical procedure, such that: 1) The analysis may be made on very small samples. 2) Reduce the time needed to make an analysis as miniaturization increases the reaction speed of the involved reagents. Such a microsystem has several significant advantages, first the use of very small amounts of toxic reagents, is an environmental advantage. Secondly the increased reaction speed will decrease the overall analysis time from hours and minutes to seconds, thus the results of an analysis is known much faster. Thirdly, the miniaturization of the analysis system makes it portable, and on-site analysis can be performed, thus removing the need for transporting the samples over long distances to a laboratory. The μTAS concept was first introduced to address issues of automatization in the field of chemical analysis, but since its introduction the use of microfluidics have expanded to many other areas within the scientific community. As a consequence of this, new terminologies have been introduced, in order to cover the wide use of miniaturized systems and devices. Today the concept of a miniaturized Total Analysis System is referred to as a Lap-On-a-Chip (LOC) microsystem. As the name indicates, the vision is to integrate an entire laboratory on a single device, which (ideally) may fit in the palm of your hand. Such devices that are small and portable would be of great benefit in medical diagnostics in remote areas or, if the device is disposable, in detection of highly infectious deceases as cross contamination would be prevented. From the beginning, the tools for fabrication of LOC devices, have been adapted from the world of micro electromechanical systems (MEMS), where the use of photolithography and etching techniques for pattern definition in silicon and other materials were well established. The adaption of fabrication techniques from the silicon world allows for a parallel fabrication of multiple devices, thus reducing the fabrication time and cost for each device. If the fabricated LOC devices are to be disposable after a single use, they need to be cheap. Therefore, LOC devices are preferably fabricated in polymers, as polymers are much cheaper than silicon. Previously polymethylmethacrylate (PMMA) and the negative epoxy based photoresist SU-8 have been used for the fabrication of LOC devices. SU-8 is easily patterned with UV-lithography and is very suitable for microfluidics. However, SU-8 has a high optical loss in the visible region and therefore it is not very suited for optical applications [2]. It should be noted that SU-8 was not
CHAPTER 1. INTRODUCTION

developed for optical applications, which is the reason for the high optical loss. PMMA has been used for optical applications for a long time, but the chemical resistance of the material is far from perfect, e.g. PMMA has been known to swell when exposed to Ethanol [3, 4]. Furthermore, PMMA is not resistant towards acids, bases or solvents [5]. Therefore it is attractive to replace these materials with other materials that matches or have better properties than SU-8 and PMMA. Recently Topas has been introduced by Ticona [6], Topas is a cyclic-olefin copolymer developed for optical and biochemical applications. Topas has a low optical loss, and is chemical resistant towards acids, bases and polar solvents. Furthermore the water uptake of Topas is much lower (<0.01%) than for other polymers, e.g. PMMA (0.3%). As Topas is thermoplastic it can be patterned by Nanoimprint Lithography (NIL) [7].

An important issue in the development of LOC devices, is the integration of on-chip light sources [8]. The need for such integrated light sources comes from the widespread use of optical detection methods such as absorbance or fluorescence. Traditional optical detection systems, that involve microfluidics, have been assembled from many different components, which have been mounted individually. Such a setup makes the entire system very sensitive towards noise, which is caused by thermal expansion and vibration in the different components [9]. Furthermore optical noise is generated at each reflection or refraction at an optical interface. To address these issues many have turned to available miniaturized components, such as LEDs and optical fibres. These components have been integrated with the microfluidic network by the so called pig tailing method, where an optical fibre is aligned to the microfluidic network, or they have simply been glued on to the microfluidic device. Such alignment and attachment steps in the fabrication will be costly and the handling of the finished devices will be hampered by the attached waveguides or LEDs. By integrating the waveguide with the microfluidic network the complexity of the system is reduced [10], but coupling to an external light source is still necessary. In general two approaches have been used to integrate light sources on LOC devices, one is the integration of silicon based light sources with a microfluidic network (usually fabricated in polymer) and the other is the integration of polymer based light sources. Polymer based light sources have the advantage over silicon based light sources that no alignment is needed, as the light source is integrated in the design phase and thus is at the desired location on-chip, without the need for alignment or hybridization.

1.1 Objectives

This project has two objectives:

1. Mature current Topas fabrication techniques and extend them to high $T_g$ Topas grades.

2. Integrate a light source on-chip, with another optical element, by the use of planar optics.

The background for the first objective is the initial experiments made by Theodor Nielsen et al. [7], who showed that it is possible to imprint in Topas grade 8007. This has been used by Daniel Nilsson et al. [76] to imprint a microfluidic dye laser in Topas grade 8007, and seal the imprinted structures with a glass lid using an intermediate layer of Topas grade 8007. Using the same Topas grade for pattern definition and as an intermediate layer in the bonding process, may limit the possibilities of the technology, as reflow of the imprinted structures may occur.
during the bonding process. Therefore it is attractive to include other Topas grades in the fabrication, as one will be able to imprint in a high $T_g$ Topas grade and seal the imprinted structures with a low $T_g$ Topas grade, thus the imprinted structures will be completely preserved during the thermal bonding process. Therefore a process recipe for imprints in high $T_g$ Topas grades need to be developed. The motivation for the second objective is to pave the way for future integrated LOC microsystems by integrating a polymer based light source with an optical element using planar optics. The integration should be oriented towards a later integration of the light source with a flowcytometer [11], which means that the requirements put on the light from the light source, must be equal to those required by an integrated flowcytometer. The integration of the light source is to take place in the design phase, and be imprinted in Topas and sealed with a Topas grade with a lower $T_g$.

1.2 Outline of the thesis

A literature survey is given in the next section, where the current state of the art within the field of integrated light sources is presented. In Chap. 2 an introduction to Nanoimprint Lithography (NIL) is given, and the rheology that governs the imprint process is presented.

A basic introduction to laser theory is given in Chap. 4 together with an introduction to waveguide theory and cutoff conditions for waveguides. Chap. 5 gives an introduction to the material used in the project i.e. the cyclic-olefin copolymer Topas. Chap. 6 presents the design and fabrication of the LOC device. The fabrication problems are also presented and discussed. Finally the results obtained with the fabricated devices are presented in Chap. 7 together with the optical setup used for the measurements, and a discussion of the results. A conclusion and outlook is given in Chap. 8, which is followed by the bibliography. A detailed fabrication scheme for the devices is presented in Appendix A.

The work done during this project has resulted in two conference proceedings that are reprinted in Appendix F and Appendix G. Furthermore the development of the Topas imprint technology platform has resulted in a journal paper written together with Ph.D. student Brian Bilenberg, which is reprinted in Appendix H.

1.3 Literature survey

This section will present the reader with a current picture of what is state of the art in the field of integration of light sources with microfluidic networks.

The survey will not cover the field of Nanoimprint lithography or microfluidics. Literature on NIL is listed in the beginning of Chap. 2. A recent review on microfluidics has been published by David Erickson et al. [12].

When you try to make a picture of the current state of integration of light sources with microfluidics it is impossible to ignore the use of LEDs. They are widely used for light sources and are mainly connected to the device by an optical fibre, which is glued on or just brought into close contact with the microfluidic device. These examples will not be covered in this survey, but a review covering the use of LEDs together with microfluidics has been published [13].
CHAPTER 1. INTRODUCTION

![Microfluidic Device Diagram](image)

Figure 1.1: (a) Side view of the device (not to scale) of a pLED integrated with a planar glass capillary electrophoresis microdevice (b) Top view of the device. 1-3 are inlets and 4-6 are outlets. The microchannels are 50 μm wide and 40 μm deep. Adapted from [15]

Some examples presented here will use LEDs, but they are either integrated monolithically into the substrate or integrated as a part of the planar structure on the device.

While searching the literature it was clear that examples of devices with truly integrated light sources was very few and rare. Thus the example presented here may be considered the current state of the art, which regards to truly integrated light sources.

Two recent reviews on integration of optics and microfluidics have may be of interest. The first one is made by E. Verpoorte [8] and the second one by K. B. Mogensen et al. [14]. It goes without saying that both reviews emphasizes that devices with truly integrated light sources is a rare thing.

1.3.1 Polymer based LED

Edel et al. [15] have integrated an organic LED made of polymers (pLED) with a microfluidic channel and used it as excitation source for microscale Capillary Electrophoresis (CE). A schematic side view of the planar structure and a top view of the device is shown in Fig. 1.1.

The microfluidic channels were etched in a glass wafer, which was sealed with a cover plate by thermal bonding, whereafter the cover plate was polished down to a thickness of 150 μm, thus the optical microscope used in the study could have a small working distance.

The organic LED is based on blue light emitting polyfluorenes. The pLED is fabricated on a patterned Indium Tin Oxide (ITO) coated glass substrate, onto which a layer of poly(3,4-ethylenedioxythiophene)/polystyrene sulfonate (PEDOT /PSS) is spin coated, in order to form a hole-injection, anode layer. The active polyfluorene emission layer is deposited from an organic solvent to a thickness of 50-100 nm by spin coating. Finally a few hundred nm thick layer of aluminum is thermally deposited and functions as cathode. The finished structure is sealed with a glass plate in an inert gas in a glove box, using an epoxy resin. The pLED emits light through the "bottom", i.e. the light exits through the PEDOT /PSS, ITO and glass. The pLED is integrated with the microfluidics by aligning and attaching the bottom glass output face of the pLED to the underside of the microfluidic device using an optical transparent glue. The pLED has an active area of 40×1000 μm, and the overall thickness of the device is about
3.5 mm. By using a mixture of 5-carboxyfluorescein and fluorescein in the microfluidic network and operating the CE-device, the separation of the two species could easily be detected. The detection limits of the device was found to be comparable to that of a similar device, when a mercury lamp is used as excitation source.

1.3.2 Monolithic silicon transducer with LED and photodetector

Misikakos et al. [15] have fabricated a monolithic silicon transducer, where a silicon avalanche diode is used as light source, and a p/n junction is used as detector, they are integrated by a silicon nitride doped optical waveguide.

The surface of the waveguide is chemically treated such that certain biological samples may bind to the surface. As these molecules have been labelled with Au-particles, the binding of molecules within the evanescent field of the waveguide, will cause an attenuation of the light, and a reduction in the measured photocurrent may be observed. The configuration of the waveguide is very interesting as the waveguide bends 90° towards the substrate for coupling to the LED and the photodiode, normally waveguide bends are in the horizontal plane and not in the vertical plane. The bends are made possible by rounded spacers, see Fig. 1.2. The transducers are fabricated in a six-mask process cycle, which includes three low pressure chemical vapor deposition (LPCVD) steps, two for SiO₂ and one for Si₃N₄, and two implantations of phosphorous and boron, for the formation of avalanche diode and the photodetector. The SiO₂ block between the spacers is created by a LPCVD deposition of SiO₂ followed by lithographic patterning and a subsequent reactive ion etching step. The spacers are created by deposition another layer of SiO₂ (2.5 μm) followed by an anisotropic plasma etch without any patterning. The waveguide is formed by deposition of the nitride by LPCVD and a subsequent patterning by UV-lithography and reactive ion etching. The avalanche diode was formed by implanting boron through the nitride film, the waveguide has vertical sections at the ends in order to ensure good coupling of light between the transducer and waveguide. The microfluidic channel is micromachined in PDMS on a glass substrate, the channel is 700 μm long, 240 μm wide and 140 μm high, and inlet holes are made in the glass substrate. The microchannel is sealed by pressing the transducer and the PDMS microchannel together.

By using standard cleanroom processes two adjacent waveguides are coated with different recognition molecules, here B-BSA and mIgG respectively. The microfluidic channel was placed so both waveguides were covered by the channel, thus a dual analysis would be possible.
CHAPTER 1. INTRODUCTION

Figure 1.3: Monolithic integrated Vertical Cavity Surface Emitting Laser (VCSEL) and photodetector. The VCSEL and photodetector is fabricated in silicon and integrated with a microfluidic device using an aspheric lens. The images are adapted from [17]

The device was pumped with a Au-anti-mIgG solution for 25 min followed by a mixture of Au-anti-mIgG and Au-streptavidin. The B-BSA coated waveguide showed no drop in photocurrent before the introduction of Au-streptavidin and the mIgG coated waveguide has a linear decrease of the photocurrent due to a slow absorption of Au-anti-mIgG, thus a multi-analyte determination system has been proved.

1.3.3 Monolithically integrated VCSEL and photodetector

Thrush et al. have monolithically integrated a laser, a photodetector and an emission filter on the same substrate [17]. The laser is a Vertical-Cavity Surface-Emitting laser (VCSEL) which emits laser light normal to the chip plane. The setup is shown in Fig. 1.3(a), where a SEM image of the optoelectronic component is shown, two interconnection lines provide contact to the VCSEL structure in the center of the photodetector. As the photodetector is placed around the laser, the sidewalls between the photodetector and the VCSEL is covered with a metal layer, in order to shield the photodetector from the radiation arising from spontaneous emission in the laser structure. The optoelectronic device is fabricated by growing the layered structure in the VCSEL and photodetector in a molecular beam epitaxy system. The contacts for the VCSEL is defined with standard photolithography and liftoff, and the outline of the laser and the photodetector is defined using standard photolithography and dry etch. The photodetector utilizes a distributed Bragg reflector as both an emission filter and an electrical contact. Due to the design of the filter, i.e. the use of materials with a high refractive index, it is possible to filter light rays over a wide range of angles, which is an advantage when operating integrated systems,
where scattered light may be incident over a large range of angles. The microfluidic channel is fabricated on a glass substrate by conventional UV-lithography and wet etching, the channel is sealed with another glass substrate, that is thinned from a thickness of 1.1 mm to 300 μm, such that the fluidic channel is in the focal point of the lens, see Fig. 1.3(b). The channel is 45 μm deep and 100 μm wide. The microfluidic channel is mounted on a chuck and the lens is aligned to the channel using micrometer controlled stages. The optoelectronic element is aligned to the lens using an \( xyz \) stage. A schematic of the sensor setup is shown in Fig. 1.3(b). The assembled device was operated with different concentrations of IRDye\(^{TM}\) 800 Phosphoramidite dissolved in methanol. A relationship between the dye concentration and the photodetector current was found, thus proving a working device.

The authors have also demonstrated the fabrication of similar sensor arrays with different sized sensors [18], thus a future integration of sensor arrays with microfluidic networks should be possible.

### 1.3.4 Optical polymer structures integrated with photodiodes

The device fabricated by Balslev \textit{et al.} differ from the previous presented devices, by the fact that the light source, here a microfluidic dye laser, emits laser light in the chip plane [19].

The integration of light source and microfluidics is made in the design phase, thus it is possible to fabricate light source and microfluidics in one lithographic step. An optical image of the device is shown in Fig. 1.4. The cuvette has two inlets and it is possible to mix two reagents before the analysis. The laser light from the microfluidic dye laser is collected by many waveguides, which makes it possible to investigate the time evolution of the sample, if mixed with a reagent. Furthermore it is possible to investigate the influence of diffusion on absorption. The fabrication makes use of the silicon substrate and the photodiodes are embedded in it. The microfluidic dye laser, optical waveguides and microfluidic network is fabricated on top of
the silicon substrate using a combination of thermally grown SiO\(_2\) and SU-8. The structures of the dye laser, waveguide and microfluidic network is patterned in a single lithographic step using conventional UV-lithography. The patterned structures are sealed with a glass lid using thermal bonding and PMMA as intermediate layer. The microfluidic dye laser is optically pumped with an external Nd:YAG laser. The LOC is operated with different solutions of xylene orange in the cuvette, and a relation between the xylene orange concentration and the current from the photodiodes was found, thus proving a working device.

1.3.5 **Vertical-Cavity Surface-Emitting laser with integrated waveguide**

Lin et al. have fabricated a Vertical-Cavity Surface-Emitting Laser (VCSEL) with a monolithic integrated waveguide. The laser structure is grown using a Veeco Applied Epi Gen III molecular beam epitaxy system on a GaAs wafer. The layered structure is shown in Fig. 1.5. The device fabrication begins with the definition of metal contacts using conventional photolithography and liftoff. The VCSEL mesas are created using conventional UV-lithography and reactive ion etching. The VCSEL-waveguide structure is operating in single mode for both the longitudinal and lateral direction. Waveguide modes are observed, but due to the design they are not lasing, and are at least 40 dB lower than the desired laser mode of the laser cavity. The device has not yet been integrated with microfluidics, but nevertheless it is presented here as an example of how the integration between light source and waveguide could be done.
Chapter 2

Nanoimprint Lithography

In this chapter a short introduction to Nanoimprint Lithography (NIL), and the NIL process will be given, and the rheology that is related to the NIL process will be introduced. The understanding of the rheology is important in order to predict the optimal imprint conditions. These parameters may include stamp topology, such as protrusion coverage, size and distribution of protrusions. Imprint time, temperature and force. Furthermore the relation between the initial thickness of the polymer film and the residual layer will be presented. The examples used to describe the rheology of polymers will to some extend be based on Poly-MethylMethAcrylate (PMMA), as PMMA has been used intensively in the NIL community since Stephen Chou et al. introduced NIL in 1995 [21]. The section about glass transition temperature, visco-elastic properties and viscosity is based on [22-24] The section about polymer flow and flow behavior is based on [25-27]. A good introduction to NIL and the flow behaviour of polymers would be [24] followed by [25] and [26]. However, a deeper understanding of the subject, i.e. polymer properties and viscosity, is not complete without [22] and [23].

2.1 NIL process

The basic NIL process is illustrated in Fig. 2.1. Before the NIL process two things has to be prepared: 1) A stamp, usually made of Silicon, where the desired pattern is fabricated as protrusions on the stamp. 2) A thin thermoplastic polymer film must be spin coated onto a hard substrate, e.g. Silicon or SiO2, the thickness of the polymer film is comparable to the height of the protrusions on the stamp. The substrate and the stamp are placed in the imprint machine and the imprint chamber is evacuated. When the chamber is evacuated the substrate and stamp are heated to a designated temperature above the glass transition temperature, $T_g$, for the polymer. When the temperature is reached, the stamp and substrate are pressed together, this is done with sufficient force and time, so the pattern on the stamp is completely transferred to the polymer film on the substrate. Cooling is initiated and the stamp and substrate are cooled to a temperature below $T_g$. The force is released and the stamp and substrate are separated, and the pattern on the stamp is now transferred to the polymer film. When the imprint cycle is finished, a residual layer is present at the bottom of the imprinted pattern. This layer is of significant interest if one wants to use the imprinted pattern for
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Figure 2.1: Basic NIL concept. a) A stamp is fabricated and a substrate is spin coated with a thin thermoplastic polymer film. b) The stamp and substrate are heated to an elevated temperature above the glass transition temperature, \( T_g \), and the stamp and substrate are pressed together with sufficient force and time, for the polymer to fill the cavities of the stamp. c) The stamp and substrate is cooled until the temperature drops below \( T_g \) and are separated. The pattern on the stamp is now transferred to the polymer film.

optical applications. The thickness of the residual layer has to be thin enough, so it is not able to guide light. If the residual layer is too thick, it is necessary to remove it by a dry etch process.

2.2 Glass transition temperature and the visco-elastic behavior of polymers

The glass transition temperature, \( T_g \) of a polymer naturally defines a point of reference for the temperature range. In polymers, \( T_g \) is the onset temperature for molecular motion [22]. In Fig. 2.2 two transitions, \( T_g \) and \( T_f \) and three flow states, glassy, rubbery and flow, are shown for a thermoplastic polymer. Below \( T_g \), the major contributor to deformation is elongation of atomic bonds in the polymer, and the deformation is elastic, i.e. it is reversible. Young’s modulus for the glassy regime is approximately constant over a wide range of polymers (~3 × 10^9 Pa), and the magnitude of the deformation is very small. Above \( T_g \), local motion of chain segments takes place and Young’s modulus drops several orders of magnitude. However, the polymer chains are still fixed in the polymeric network due to entanglements. Beyond \( T_g \), a rubber-elastic plateau exists where relative large deformations can take place, due to elongation of chain segments, which are fixed between entanglements points. Any deformations in the rubbery state will, to some extent, recover after the force is released. The width of the rubbery state depends on the molecular weight, if the molecular weight is very low, no rubber-elastic plateau is found. When the temperature is elevated above \( T_g \), the flow state is reached. In this regime motion of entire chains may take place. The modulus and the viscosity are further reduced in this region and deformations are irreversible, thus making it an optimal state for NIL. It is empirical found, that an optimal temperature for NIL is found 70-80 °C above \( T_g \) [24].
2.3 Viscosity

In NIL one of the most important parameters is the viscosity, \( \eta \), of the polymer. The viscosity represents the resistance to flow, and can be looked upon as a measure of frictional forces. For polymers, the frictional forces are due to entanglement of the polymer chains, and the friction involved in polymer chains sliding back and forth. Friction can also come from bond stretching in the polymer chain. For newtonian fluids there is a linear relation between the shear stress and the shear rate, thus giving a constant viscosity. For low shear rates this is also the case for non-newtonian fluids. For high shear rates non-newtonian fluids experience either shear thinning or shear thickening. For shear thinning the viscosity decreases for increasing shear rates, and for shear thickening the viscosity goes up for increasing shear rates. Liquids that are shear thinning or shear thickening are often referred to as pseudoplastic or dilatant respectively.

For newtonian and non-newtonian fluids the viscosity is defined as the ratio between the imposed shear stress, divided by the shear rate,

\[
\eta = \frac{\text{shear stress}}{\text{shear rate}} = \frac{\tau}{\dot{\gamma}} \tag{2.1}
\]

The viscosity is typically measured by a rotating plate geometry, and the measured viscosity can be plotted as a function of shear rate. In Fig. 2.3(a) such a plot is shown, it is referred to as a viscosity shear curve. The plot contains two regimes, a regime at low shear rates with a constant viscosity, called the zero shear rate viscosity, \( \eta_0 \), and a regime at high shear rates, where the viscosity is decreasing linearly as the shear rate increases. Such curves are described by a truncated power law model \[23\],

\[
\eta(\dot{\gamma}) = \begin{cases} 
\eta_0, & \dot{\gamma} < \dot{\gamma}_0 \\
\frac{\eta_0}{\eta_0 \left( \frac{\dot{\gamma}}{\dot{\gamma}_0} \right)^k}, & \dot{\gamma} > \dot{\gamma}_0
\end{cases} \tag{2.2}
\]

where \( k \) is a constant, \( \eta_0 \) is the zero shear rate viscosity and \( \dot{\gamma}_0 \) is the limiting shear rate, which describes the transition from a constant value to the power law model. This model is shown.
in Fig. 2.3(a), where the two curves A and B represents the viscosity of a polymer at two different temperatures. Another model, the Carreau-Yasuda model, is often used to describe the viscosity over the entire shear rate range. The Carreau-Yasuda model reads

\[ \eta = \eta_0 (1 + (\dot{\gamma}/\tau)^a)^{n-1} \quad (2.3) \]

where, \( \eta_0 \) is the zero shear rate viscosity, \( \tau \) is a time constant, \( n \) is the "power-law exponent" as it describes the slope in the power region, and \( a \) is a dimensionless parameter that describes the transition region between the zero-shear rate region and the power-law region. For many polymer solutions and melts, good fits can be obtained for \( a=2 \). When \( a=2 \) in Eq. (2.3) it is usually referred to as the Carreau equation, as the parameter \( a \) was added later by Yasuda [28].

The viscosity of polymers are influenced by many parameters, such as temperature and the molecular weight of the polymer. A high molecular weight indicates large molecules, and therefore it becomes more difficult for the chains to slide back and forth. The addition of either additive or filler to the polymer solution will also influence the viscosity, as will the external pressure. The influence of these parameters are summarized in Fig. 2.3(b). It is shown, that the viscosity is very dependent on the temperature, as a small increase in temperature, like 10 K, could decrease the viscosity by almost an order of magnitude [22]. The influence on the viscosity by the molecular weight, \( M_w \), is given by [30]

\[ \eta_0 \propto \begin{cases} M_w & , M_w < M_c \\ M_w^{3.4 \pm 0.2} & , M_w > M_c \end{cases} \quad (2.4) \]

where \( M_c \) is the critical molecular weight. \( M_c \) can be interpreted as the molecular weight where the polymeric network, and the entanglements, spans macroscopic dimensions. Below
Figure 2.4: Zero shear rate viscosity of PMMA for three molecular weights, $M_w$, is measured at different temperatures. The graph shows the influence of the molecular weight and temperature, respectively. WLF stands for William-Landel-Ferry. (Adapted from [23])

$M_c$ entanglements may be formed, but their number are too low to form a connected network. Therefore the polymer solution or melt, has flow properties that resembles that of low molecular weight compounds and the viscosity is linearly proportional to $M_w$. Above $M_c$ the polymer chains are longer, and there are enough entanglements in the polymer melt to form a connected network [22]. The influence of temperature on the viscosity is described by the empirical Vogel-Fulcher law [30]

$$
\eta_0(T) = B \exp\left(\frac{-T_A}{T - T_V}\right)
$$

where $T_A$ is the activation temperature, and $T_V$ is the Vogel temperature. The Vogel temperature lies about 50 K below $T_g$ and refers to the temperature at which the flow processes actually cease. The flow processes between the Vogel temperature and up to a few degrees below $T_g$ have not ceased, they are just extremely slow [22]. The influence of molecular weight, $M_w$ and temperature is shown in Fig. 2.4, where the zero shear rate viscosity is plotted for PMMA for three molecular weights, as a function of temperature.

### 2.4 Squeeze Flow

In Fig. 2.5 a simple model for the description of squeeze flow during imprint is presented. The model is an idealized model and describes the polymer flow in one dimension. The stamp consists of $N$ parallel lines, with length, $L$, height, $h_r$, and width $s$. The distance between the protrusions is $w$. The initial height of the polymer film is $h_0$.

In order to describe the flow of the polymer, some assumptions needs to be made. We consider the polymer, when heated to elevated temperatures, as a purely viscous fluid, that
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Figure 2.5: Geometrical definitions used for the description of squeeze flow during imprint. **left:** The initial conditions before imprint. **right:** Conditions during imprint, the polymer moves from underneath the protrusions into the cavities, and the polymer velocity profile has the well known parabolic shape. The polymer always flows towards the nearest cavity.

means that the elastic properties of the polymer is ignored. Furthermore the polymer is regarded as a Newtonian fluid, this implies that the flow velocity is parabolic and that the velocity is zero at the walls, and maximum at the center of the flow. The viscosity, $\eta$, is constant and is set to the zero shear rate viscosity, $\eta_0$. The polymer is incompressible and no air is trapped between the stamp and the substrate. The characteristic size of the polymer molecule is much smaller, than the size of the stamp protrusions and the initial thickness of the polymer film.

During the imprint process, a force, $F$, is applied and the polymer begins to flow under the pressure applied by the protrusions. The polymer flows towards the nearest cavity, and therefore the polymer that fills the cavity $w_i$, flows in from the right side under protrusion $s_{i-1}$ and from the left side under protrusion $s_i$. If we assume complete filling of the stamp, the height of the imprinted pattern is $h_f$, and the thickness of the residual layer is $h_r$. By applying the continuity equation, and keeping in mind the polymer is considered incompressible, we get:

$$
 h_0 \sum_{i=1}^{N} (s_i + u_i) = h_f \sum_{i=1}^{N} (s_i + u_i) + h_r \sum_{i=1}^{N} u_i
$$

(2.6)

the index, $i$ refers to a single protrusion or cavity. The summation provides the result for the entire stamp. By rewriting Eq. (2.6) it is possible to find a relation between the initial thickness of the polymer film, the protrusion coverage and the thickness of the residual layer.

$$
 h_r = h_0 - h_f \left[ \frac{1}{\Lambda} \sum_{i=1}^{N} u_i \right], \quad \Lambda = \sum_{i=1}^{N} (s_i + u_i)
$$

(2.7)

Here the term inside the square bracket is known as the Protrusion Coverage (PC), which is the ratio of the stamp that is covered with protrusions. Stamps that have a PC below 0.5 are called positive, and stamps with a PC above 0.5 are called negative. The flow of incompressible fluids are governed by the Navier-Stokes equation for incompressible fluids [31]

$$
 \rho \left( \partial_t \mathbf{v} + (\mathbf{v} \cdot \nabla) \mathbf{v} \right) = -\nabla p + \eta \nabla^2 \mathbf{v} + \mathbf{F}_{\text{body}}
$$

(2.8)

here the two components on the lefthand side accounts for the time evolution of the system and the inertial forces respectively. On the righthand side three components are present, $-\nabla p$
accounts for the pressure drop along the polymer film and $\eta \nabla^2 \mathbf{v}$ are viscous forces in the system. $\mathbf{F}_{\text{body}}$ account for the gravitational forces on the polymer film.

As the polymer film is very thin, the gravitational force is equal over the entire wafer and therefore it has no influence on the polymer flow, furthermore we assume the flow is quasi-stationary. This reduces the Navier-Stokes equation to

$$\nabla \mathbf{p} = \eta \nabla^2 \mathbf{v}$$

where the pressure gradient equals the viscous forces. By following the derivations in [23] it is possible to find the imprint time, $t_f$, for an imprint with complete filling of the stamp

$$t_f = \frac{\eta_0 L s^3}{2F} \left( \frac{1}{h_f^2} - \frac{1}{h_0^2} \right)$$

It is worthwhile to sum up the conclusions from Eq. (2.10), as it shows the strong influence on the imprint time, that the size of the protrusions has. A doubling of the width, $s$, of the protrusions will lead to a 16-fold increase in imprint time, when other parameters are constant. The imprint force only has a weak influence on the imprint time, as $t_f \propto \frac{1}{F}$. The viscosity has similar weak influence on the imprint time, as $t_f \propto \eta$. However, it is possible to change the viscosity significantly by changing the temperature, so a small increase in temperature may lead to shorter imprint time, when other parameters are constant. The filling of a cavity as a function of time is shown in Fig. 2.6 where the imprint gradually slows down when the cavity is filled. When the cavity is completely filled the imprint will continue, if the force and temperature is still applied, but at a much slower rate.

2.5 Polymer flow during imprint

In Fig. 2.6 the filing of a cavity, as a function of time is shown, from that image it could be interpreted that the polymer slowly fills the cavity from beneath, until it reaches the bottom of the cavity. This is not entirely true, as the polymer flow inside a cavity, is a bit more sophisticated. When the stamp and substrate are pressed together, the polymer between
them is squeezed and therefore a lateral transport of polymer takes place toward the nearest cavity. An illustration of this is shown in Fig. 2.7, where a schematic illustration shows the polymer flow in a partially filled cavity. It can be seen that two effects take place. 1) The polymer that flows into the cavity from the sides, flow up the cavity walls, indicating a capillary effect. 2) A deformation of the central region is observed, and the polymer that are in the cavity prior to the imprint process, is compressed by the incoming polymer, which results in a bowing of the central region. The polymer in the central region and the incoming polymer does not mix, and a narrow groove separates the two regions, this groove is clearly seen in the AFM height profile in Fig. 2.7.

As mentioned earlier in this chapter, the protrusion coverage is important for the imprint process. It has been shown that small cavities are filled much faster than large ones, and that small cavities, when filled completely, form larger protrusions with the protrusions surrounding them. This increases the effective protrusion coverage of the stamp and will slow down the imprint. If the protrusions are not evenly distributed across the stamp, the local variations in PC, will results in a different imprint time for the different areas of the stamp. Furthermore this will result in an uneven residual layer thickness, and if the pattern is used for pattern transfer, this puts some restrictions on the process. This is illustrated in Fig. 2.8(b), where the central region of a negative stamp has lots of cavities and therefore a smaller protrusion coverage. The central region will have a shorter imprint time than the boundaries. A transition region is observed between the cavities and the boundaries, thus giving an uneven thickness of the residual layer. For a typical stamp made from a 500 μm thick four inch silicon wafer, transition regions of several 100 μm has been observed [23]. In order to minimize stamp bending one could introduce a flexible stamp that adapts for any inhomogeneities in the protrusion coverage and defect on the substrate and produces a highly homogenous residual layer [32]. If this is not possible one usually arrange the patterns on the stamp in a symmetrical manner.
(a) The influence of the effective protrusion size is illustrated by bars. a) only the stamp protrusions are in contact with the polymer b) The smallest cavities are filled, and as the cavities are filled they effectively form large protrusions, thus increasing the imprint time, see Eq. (2.10) c) the large stamp cavities are filled d) full contact between stamp and polymer. (Adapted from [25])

(b) Schematic view of the imprint of an nano-structured array surrounded by large protrusions. 1) stamp 2) resist before imprint 3) local bending of stamp due to differences in protrusion coverage 4) resist after pattern transfer 5a) to 5c) shows different states of pattern transfer. 5b) is the state where complete pattern transfer is possible. (Adapted from [23])

Figure 2.8: Filling of stamp cavities and the bending of stamp due to local differences in protrusion coverage.
2.6 Example: Imprinting in Topas grade 8007

The final section will investigate if the assumption of a constant viscosity is justified, when imprinting in Topas grade 8007. The shear velocity relation is given in [23] and is found to be

\[
\frac{dv_y}{dz} = \dot{\gamma}_{xy} = \frac{12F}{\eta_0 L s^3 yz} \tag{2.11}
\]

by solving Eq. (2.11) with respect to \( z \) we get

\[
|z(y)|_{\dot{\gamma}_{xy}} = \dot{\gamma}_0 = \frac{\eta_0 L s^3}{12F} |y^{-1}| \tag{2.12}
\]

here \( \dot{\gamma}_{xy} = \dot{\gamma}_0 \), as \( \dot{\gamma}_0 \) limits the valid range for the assumption of constant viscosity. The shear rate is at a maximum at the corners of the stamp protrusions, where \( y = \frac{L}{4} \) and \( z = \frac{b_0}{2} \).

The model system is made of an array of parallel protrusions, which is comparable to the laser cavity fabricated in this project, see Sec. 6.1.3. The laser cavity is made of 21.5 \( \mu \)m wide and 1000 \( \mu \)m long protrusions. Topas grade 8007 has a zero shear rate viscosity of, \( \eta_0 = 3600 \) Pa s at 200 °C. The force under a single protrusion is calculated to 2.3 N. By using these parameters in Eq. (2.12) it is possible to calculate the maximum film thickness, if the limiting shear rate, \( \dot{\gamma}_0 \) is not to be exceeded. Calculation yields

\[
|z(10 \mu m)|_{\dot{\gamma}_{xy} = \dot{\gamma}_0} = (2s)^{-1} \frac{3600 \text{Pas} \times 1000 \mu \text{m}^{(21.5 \mu \text{m})^3}}{12 \times 2.3 \text{N}} |10 \mu \text{m}|^{-1} = 2.57 \AA \tag{2.13}
\]

This provides a maximum film thickness of 5.14 Å, if the limiting shear rate is not to be exceeded. The polymer film imprinted in this project is 10 \( \mu \)m thick and therefore the assumption, that the shear rate is below the limiting shear rate not fulfilled. The polymer will therefore experience shear thinning, thus leading to a lower viscosity during the imprint process. However, the squeeze flow will not be affected, and the polymer flow during the imprint process remains as explained in Sec. 2.5. The fact that the Topas polymer experience shear thinning may very well be the reason, that we are able to imprint large structures into Topas.
Chapter 3

Surface coatings for Nanoimprint

This chapter will briefly describe adhesion and two fabrication techniques for surface coatings will be presented. Furthermore a small review of some of the systems for fabrication of silane based anti-sticking coatings will be made.

A comparison of the three different anti-sticking coatings that have been fabricated and tested in this project will be presented and compared. The weight of the investigation will be on the plasma deposited $C_4F_8$ coating and the commercially available $F_{17}$TCS coating.

3.1 Introduction

In Nanoimprint Lithography (NIL) adhesion is a very important parameter, and to have a working NIL-process the adhesion must be controlled. Adhesion is important at two interfaces, between stamp and polymer and between polymer and substrate. It is clear that strong adhesion between polymer and substrate is required as well as weak adhesion between stamp and polymer. In most NIL processes the stamp and substrate are made of the same material, e.g. silicon or SiO$_2$, thus matching the thermal expansion of stamp and substrate. When both substrate and stamp are made of the same material it is difficult to ensure a strong adhesion between substrate and polymer and a weak adhesion between polymer and stamp, as the adhesion between polymer and silicon or SiO$_2$ is good as long as the silicon or SiO$_2$ is clean and dry.

Strong adhesion between substrate and polymer, is usually achieved by cleaning the substrate and baking it at elevated temperatures, before the polymer is spin coated onto the surface. The adhesion between stamp and polymer is usually weakened by applying an anti-sticking layer to the stamp. The anti-sticking layers used in NIL are usually fluorocarbon based, and can be deposited by plasma deposition [33], by liquid phase deposition [34] or by vapor phase deposition [35]. Currently the most wide spread method in the NIL community is vapor phase deposition.

The motivation for the investigation of different anti-sticking coatings is the limited durability of the $C_4F_8$ based anti-sticking coating, which has previously been used at MIC. The coating has to be renewed after two to four imprints, thus limiting one of the advantages of NIL. Furthermore the first experiments with Topas grade 5013 indicates that the $C_4F_8$ based
coating is not good enough to ensure a release of the stamp after being imprinted into this Topas grade. Therefore a crucial step in developing a recipe for imprints in Topas grade 5013, and other high $T_g$ Topas grades, is the introduction of a better anti-sticking layer.

### 3.2 Adhesion

The strength of the adhesion between two materials are given by the work required to separate them. The adhesion energy is given by the difference of the surface energy of the materials, i.e. silicon and polymer, to air and the surface energy of them in contact. This is illustrated in Fig. 3.1 The adhesion energy is defined as

$$ W_{adh} = (\gamma_p + \gamma_s) - \gamma_{ps} $$

(3.1)

where $\gamma_s$ and $\gamma_p$ are the surface energy of silicon and polymer in air respectively and $\gamma_{ps}$ is the surface energy of the interface between silicon and polymer. When the surface energies of the two materials in air are known, it is possible to estimate the surface energy of the interface between them by using an often used approximating [36]

$$ W_{adh} = (\gamma_p + \gamma_s) - (\sqrt{\gamma_p} - \sqrt{\gamma_s})^2 $$

(3.2)

The surface energy of a solid material is determined by the contact angle method. A definite drop of a known liquid is placed on the material, and the contact angle is measured. The definition of the contact angle, $\delta$, is shown in Fig. 3.2, when the contact angle is below $90^\circ$, one refers to a wetting situation, and when $\delta$ is above $90^\circ$ one refers to a dewetting situation. The measurements of the contact angle relies on an equilibrium between solid, liquid and air, which can be described by Young’s equation

$$ \gamma_l \delta = (\gamma_s - \gamma_{sl}) - (\gamma_h - \gamma_{hv}) \approx (\gamma_s - \gamma_{sl}) $$

(3.3)

where $\gamma_l$ is the known surface energy of the liquid, $\gamma_h$ is the unknown surface energy of the solid, and $\gamma_{sl}$ and $\gamma_{hv}$ are the interfacial energies of the solid to liquid and air respectively. In
order to extract the unknown surface energy of the solid, at least two data points must be available \((\delta_1, \gamma_1; \delta_2, \gamma_2)\), thus one has to use at least two known liquids with different surface energies. The data points are plotted and used for an extrapolation towards complete wetting, where \(\delta\) will be zero, and the interfacial energy between the liquid and the solid will tend to zero, thus \(\gamma_3\) is easily extracted. The extrapolation is shown in Fig. 3.2. When measuring the surface energy of solids, the surface needs to be completely flat, as the surface roughness has a significant influence on the contact angle.

### 3.3 Fluorocarbon-based coatings deposited by plasma deposition

The plasma deposited anti-sticking layer is based on the passivation layer used in Deep Reactive Ion Etching (DRIE)-tools. It was suggested by Ayón \textit{et al.} \cite{33} to deposit a few monolayers of PTFE-like fluorocarbon polymer as anti-sticking coating, and it has previously been widely used as an anti-sticking layer in the NIL community. The anti-sticking coating is deposited from a \(\text{C}_4\text{F}_8\) precursor gas, which is dissociated by plasma to form ions and radical species \cite{37}

\[
\text{C}_4\text{F}_8 + e^- \rightarrow \text{CF}_x^+ + \text{CF}_x^- + \text{F}^- + e^- \quad (3.4)
\]

the dissociated species then polymerize on the surface and forms a layer of polymerized \(\text{nCF}_2\) on the surface

\[
\text{CF}_x^- \rightarrow \text{nCF}_2 \quad (3.5)
\]

The thickness of such a fluorocarbon film has been measured to be around 5 nm \cite{38}. Fig. 3.3 shows a SEM image of the surface of a stamp coated with a \(\text{C}_4\text{F}_8\) based coating, and it is seen how the fluorocarbon polymer forms a polymerized network on the surface of the stamp, thereby leaving parts of the stamp uncoated. Increasing the deposition time, and thereby the thickness of the polymerized layer of \(\text{nCF}_2\) is not an option, if one intent to make nanostructured imprints, as a thick anti-sticking coating will reduce the good dimension control of the NIL process. The nature of the fluorocarbon film is that it has a rather weak adhesion to the stamp and therefore the durability of the coating is limited. It has been
reported that the amount of fluorine in a C₄F₈ based coating is decreasing as the stamp is reused [39], thus the anti-sticking layer will slowly lose its anti-adhesive properties as the fluorine is removed. When used under normal NIL conditions the fluorocarbon coating last for a few imprint, usually two to four depending on the structures on the stamp and which thermoplastic that is imprinted.

3.4 Fluorocarbon chains deposited by liquid or vapor phase deposition

In order to address the durability problem of the plasma deposited coatings other methods for deposition of anti-sticking layers have been proposed. A very promising technique is deposition of fluorocarbon chains of varying length, they are attached to a silane head group, that binds covalently to the surface of the stamp. Two methods for deposition of these silane-based fluorocarbon films exist, a liquid phase deposition [34] [40] and a vapor phase deposition [41] [35]. The liquid phase deposition has some obvious disadvantages when used on stamps with nm-sized structures, as discussed by Beck et al. [35]. When a stamp is submerged into a liquid solution, the stamp is not completely covered, as the liquid is not wetting the hydrophobic stamp completely, this is illustrated in Fig. 3.4, where the black markings show areas of the stamp not covered by the anti-sticking coating. This insufficient wetting effect is dominating stamps with nm-sized protrusions as the effect is not as critical for stamps with µm-sized protrusions. The vapor phase deposition has the advantage that it does not experience incomplete wetting problems during deposition. Furthermore it has been reported that vapor phase deposition gives a slightly lower work of adhesion than similar coatings deposited by liquid phase deposition [41].

The silanization process is suggested to proceed in the following way [36] and is illustrated in Fig. 3.5. 1) The oxidized silicon surface has adsorbed a thin water film, and the silane head groups are adsorbed to the water layer by physisorption. 2) The hydration of the chlorosilane head groups where the Cl atoms are exchanged with OH groups under reaction with water to hydrochloride acid. The thin initial layer of water allows the molecules to move laterally on the surface, which leads to a reorganization of the monolayer. By controlling the temperature at
Figure 3.4: Illustration of wetting defects on NIL-stamps with different sized protrusions, during liquid phase deposition of an anti-sticking layer. The silanes used for anti-sticking layers are soluble in hydrophobic liquids like hexane which does not have sufficient wetting capabilities on NIL-stamps with nm-sized protrusions. The incomplete wetting is illustrated by the black areas, and these areas of the stamp functions like a stamp with no anti-sticking coating, thus giving severe adhesion problems during imprint. (Adapted from [35])

At this stage, it should be possible to form densely packed monolayers of vertical chains of organic molecules. 3) Polymerization, where the siloxane molecules become laterally linked together through oxygen atoms. Some covalent bonds are also created to the surface, thus linking the polymeric network to the silicon. The coverage of the anti-sticking coating depends on the number of OH groups on the silicon surface, so the amount of absorbed water on the surface must be controlled. If too much water is absorbed, the anti-sticking coating will polymerize on top of the water film, without bonds to the surface.

3.5 Review of VPD systems

Different vapor phase deposition systems and the equipment needed for the fabrication of silane based anti-sticking coatings are shortly described.

Molecular Vapor Deposition by Applied Microstructures

This commercially system is supplied by Applied Microstructures [42]. The systems allows for a precise deposition of a monolayer of organic molecules on a substrate, hence the name: Molecular Vapor Deposition (MVD). The system consist of a temperature controlled deposition chamber, which has a built in plasma source for cleaning and oxidizing the surface. The system comes with an advanced multi-precursor delivery system, that effectively controls the delivery of precise doses of precursors and catalyst vapors into the deposition chamber. A schematic of the system is shown in Fig. 3.6

**Pros:** Allows complete control over the process parameters and very durable and dense anti-sticking layers are fabricated. Furthermore the process is fully optimized.

**Cons:** The only major drawback is the price tag, as such a machine is quite expensive.
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Figure 3.5: Illustration of the formation of an anti-sticking layer on an oxidized silicon surface. a) physisorption to the thin water film on the surface b) hydration of the siloxane under HCL formation (Not shown) and polymerization of the anti-sticking layer c) creation of covalent bonds to the surface and water release (Adapted from [36])

Figure 3.6: Schematic of the Molecular Vapor Deposition system (MVD). The MVD system has an integrated plasma source that allows for an uniform hydroxylation of the surface prior to coating. An advanced delivery system allows for precise dosage of precursors and catalyst vapors in the deposition chamber (Adapted from [43])
Glow box model

This homebuilt setup, which is shown in Fig. 3.7, is the simplest VPD setup know to the author. The stamp to be coated is placed on a hotplate and a petri dish is placed up side down on top of it. The petri dish and stamp are heated to 250 °C, which is well above the boiling point for silane solutions, i.e. 192 °C. A drop of silane solution is manually dispensed through a small injection hole in the petri dish. The hole is covered and as the silane evaporates in the petri dish a silane atmosphere is created, thus coating the surface.

Pros: The simplicity makes the system very durable, as no mechanical problems will occur. The price tag of this setup is limited to a hotplate, a petri dish and the silane solution, and hotplates and petri dish’s are usually standard equipment.

Cons: The setup does not allow for much control of the process parameters, except temperature. The manually dispensation of the silane, may result in to much silane being injected and the fluorocarbon chains may polymerize on top of the stamp, thus creating areas with visible defects.

This glow box setup is a cheap approach to vapor phase deposition, as it requires a very little amount of investment in equipment. This approach is known to be used at Tyndall (Ireland), at Lund University (Swden) [35] and at University of Wuppertal (Germany) [44]

Home made VPD-chamber

This system is made of a vacuum chamber, a membrane pump and a pressure gauge. The chamber is supplied with an Argon and a Nitrogen inlet, thus it is possible to create a inert atmosphere at low pressures in the chamber. The silane is injected through a septum using a syringe, due to the low pressure in the chamber, the silanes evaporates completely when injected.

Pros A better control over pressure, amount of injected silane and atmosphere than for the glow box setup. Furthermore an optimization of the parameters are possible here due to
CHAPTER 3. SURFACE COATINGS FOR NANOIMPRINT

the pressure gauge and injection needle, furthermore the system is much cheaper than
the commercially available system from Applied Microstructures.

Cons The injection system is not so sophisticated as the one used on the commercial sys-
tem, and it is not possible to control the temperature. Furthermore the system is not
automatized as all actions are manually initiated.

Such a system has been implemented by Helmut Schifft at the Paul Scherrer Institute in
Switzerland [45]

Conclusion

The best technical solution is a machine from Applied microstructures, followed by the home-
built anti-sticking chamber and last the glow-box setup. What may be the best solution for a
research department depends on many parameters. If money is not an issue, one should buy
the machine from Applied Microstructures, but if money is a limiting factor, the choice de-

dpends on the available man power of the research department. A small department may choose
the glow-box setup, as it requires very little man power to assemble, whereas a larger research
department may initiate the construction of a homemade anti-sticking chamber. In this case
money was a limiting factor, but luckily the research department at MIC is quite large, so it
was not a problem to initiate the construction of a homemade anti-sticking chamber.

3.6 Homebuilt chamber for VPD

As part of this project a chamber for vapor phase deposition of anti-sticking coatings has
been designed and constructed. The construction was initiated as it seemed impossible to
finance the acquisition of a commercial MVD system within the next few years, furthermore
the homebuilt VPD system could be built by spare parts already present at MIC and Danchip,
thus keeping the price down. The chamber has been constructed at the Danchip workshop and
the only costs were the salaries for the people in the workshop and a new pressure gauge that
could measure the pressure of an Argon atmosphere. The coating machine has been designed
to meet the requirements for making VPD of anti-sticking coatings, e.i. the ability to control
the pressure, atmosphere and amount of injected precursor gas. The chamber should also be
easy to operate as it eventually will be used by several people at MIC and Danchip. An image
of the chamber is shown in Fig. 3.8. The setup is placed on a moveable rack, which make it easy
to move the setup. Starting from the top the setup has two standard electrical switches, one for
the membrane pump and one for the pressure gauge. Underneath the electrical switches, two
valves (A4Q88 from Tesco) and a switch (Norgren, 3/2 spool valve, 03 0403 02) are placed. The
valves control the injection of Nitrogen and Argon respectively, thus it is possible to flush the
chamber with Nitrogen or Argon. The switch controls which valve that is active, thus only one
valve is active at a time. The chamber is made of stainless steel, and has been fitted with pipes
and sealings so it fits the purpose of anti-sticking chamber. Stainless steel is used as it has been
reported that chambers made of softer materials corrode within a few months, when exposed
to the chemistry involved in this process [46]. The pressure in the chamber is measured with a
pressure gauge (ASG 1000mbar from Edwards) and displayed on the front of the setup. Access
to the chamber is allowed through a lid in the front, this allows for a horizontal loading of the stamps to be coated, thus safe handling of the stamps are ensure during the entire process. At the right hand side of the chamber a small inlet is fitted with a septum (11.0 mm, Z16,727-4 from Aldrich). The silane solution is injected though the septum using a precision syringe (Hamilton 705N), the septum may be reused multiple times as the punched holes in the septum are self closing. The chamber is connected to a membrane pump (Vacuubrand MD4TC) by a valve. A dead end is connected to the tube connecting the chamber and pump, in order to collect any particle that accidently may get into the tube, such that the membrane pump is unharmed. The reason for using a membrane pump instead of a conventional roughing pump, is to avoid oil vapors in the chamber, as roughing pumps are known to inject small traces of oil vapor into the chamber they are connected to. As the chamber is dedicated to anti-sticking coatings it is essential that the chamber is free of contaminants as they may influence the coating process, furthermore the chamber was cleaned thoroughly before the being taken into use, using cleanroom wipers and ethanol. It goes without saying that the atmosphere in the chamber was changed several times to ensure no ethanol vapors were present. The membrane pump is connected to the exhaust in the cleanroom and placed on a flexible mattress to reduce vibrations in the setup. A schematic diagram of the anti-sticking coating chamber is found in Appendix B. A detailed operating manual for the homemade anti-sticking chamber is found in Appendix C.

3.7 Experimental setup

In order to test and benchmark the different anti-sticking coatings, flat stamps are prepared and imprinted into different Topas grades. Flat stamps are not as critical to imprint as structured stamps, but nevertheless they are used in order to minimize the amount of processing needed to fabricate the stamps. It is possible to extrapolate the separation of a flat stamp to a structured stamp, i.e. if a flat stamp is very hard to separate for a given set of parameters, one would properly have difficulties separating a structured stamp under similar conditions. The flat stamps are made of silicon wafers, which are cleaned in HF-buffer for 30 s and rinsed in DI-water prior to coating.

C₄F₈ plasma deposited coating

The temperature of the DRIE-tool is set to 20 ºC. The stamp is loaded and exposed to an oxygen plasma for 3 min. The stamp is backside cooled with helium during the entire process. The stamp is then exposed to a C₄F₈ plasma for 30 s and an approximately 5 nm thick layer of polymerized nCF₂ is deposited on the surface.

F₁₇TCS coating

These stamps are not processed at MIC, but at Applied Microstructures, so the exact processing parameters are not entirely known. The stamp is treated with an oxygen plasma prior to coating, thus cleaning the surface and ensuring a good hydrolaxation. The perfluorodecyl-tridlorosilane precursor and catalyst vapors are injected and the wafers are exposed to the
Figure 3.8: 1 Electrical switches. 2 Valves for Argon and Nitrogen. 3 Regulator, such that only one gas may be flushed through the chamber at once. 4 Display, shows the pressure in the chamber in mbar. 5 Chamber, the stamp to be coated is placed on a petri dish turned upside down. 6 Pressure gauge. 7 Septum, here shown with a syringe through it. 8 Valve to pump. 9 Dirt collector. 10 Membrane pump. 11 Flexible mattress, used to protect the setup from vibrations from the membrane pump.
Figure 3.9: Illustrating the setup used inside Thyra and the EVG imprinter respectively. A. The setup used in Thyra, The substrate is placed as close to the bottom hot plate as possible, thus insuring a good temperature control. The PDMS is molded to a dummy wafer and placed on top of the stamp. The A sheet of tin foil is placed at the top and bottom of the setup. B. The setup used in the EVG imprinter. The substrate and stamp is placed in the center of the setup the graphite sheets are placed closest to the chuck. A layer of tin foil is placed between the substrate and stamp and the graphite sheets.

vapors for approximately 5 to 10 min.

**F$_{13}$TCS based coating**

Prior to coating the stamp is treated with an oxygen plasma in a DRIE tool. The oxygen plasma treatment is identical to the one given prior to deposition of the C$_4$F$_8$ based coating. The stamp is placed in the homebuilt anti-sticking chamber and an inert low pressure atmosphere is created. The silane is injected and the stamp is exposed to the vapors for 10 min. Then the chamber is flushed with Argon and Nitrogen respectively. A detailed operating manual is found in Appendix C.

**Preparation of substrates**

The substrates are prepared by dissolving Topas in toluene and spin coat it onto silicon wafers. The silicon wafers have been cleaned for 10 min in 7 UP and rinsed in water prior to spin coating. The wafer is heated to 150 °C for 10 min immediately before the Topas is applied. The Topas is spun onto the substrate using a speed of 2000 rpm for 60 s. After the spin process the Topas coated wafer is baked at 150 °C for 10 min, so the toluene is removed.

**Imprint setups**

Two different imprint setups are used through the project. Initially all imprints were made in Thyra, a homebuilt imprint machine [47], and later the imprints were made in a EVG 520 imprint machine [48]. The setup inside Thyra and the EVG imprinter are a bit different, but nevertheless the two machines produce identical imprints. The two setups are shown in Fig. 3.9. The major difference is the material used for the flexible mattress. In thyra a thick PDMS layer is molded and used as mattress together with a dummy wafer. In the EVG imprinter two thin graphite sheets are used. The stacked sandwich in the EVG imprinter is therefore a bit thinner than the one used in Thyra.
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3.7.1 Equipment used for estimating the surface energy

Before the stamps are used, the anti-sticking coating is evaluated by measuring the contact angle on the anti-sticking coated surface, with regards to a droplet of deionized water. During this project two different methods have been used, and in each case 10 independent measurements are made on every stamp.

The first method is based on the half-angle method [49] and was measured using a contact angle meter from Tantec. This method will be denoted Method A and the equipment used was owned by a startup company, and during this project they moved to their own facilities and therefore the equipment was no longer available at MIC. The second method, denoted Method B, uses the Sessile drop method, which is an optical contact angle method. The angle between the baseline of the drop and the tangent at the drop boundary is measured, and the Laplace-Young approximation is used to calculate the contact angle of a drop of DI-water on the surface. The measurements are made on a Krüss DSA10 [50].

3.8 Results

C₄F₈ based coating

Four imprints are made at different temperature into Topas grade 5013. The reason for this is to investigate if the imprint temperature has any influence on the breakdown of the C₄F₈ anti-sticking coating. The temperature vary from 170 °C up to 200 °C in 10 °C steps. Other imprint parameters are constant. See Appendix A for details.

It was possible to separate the imprint made at 170 °C into Topas grade 5013. A subsequent investigation of the stamp and substrate showed that only 75 % of the polymer surface had been in contact with the stamp, thus complete contact was not achieved, furthermore traces of polymer was found on the stamp, indicating adhesion problems. The next three imprints into Topas grade 5013, all had severe adhesion problems. For the imprint at 190 °C it was possible to separate stamp and substrate, and as seen in Fig. 3.10 strong adhesion between polymer and stamp is observed. For the other two imprints it was completely impossible to separate the stamp and substrate. It was suggested that the separation would be improved by adding a few hundred ppm of ZinkSterate (ZnSt) to the Topas solution [51]. ZnSt is a powerful release agent, which is widely used in injection molding as an additive to the polymer, thus improving the release from the mold. The addition of ZnSt to the Topas solution did not improve the separation of the C₄F₈ coated stamp. Furthermore the ZnSt seemed to form small visible crystals in the polymer film, thus degrading the optical properties of the Topas. A single imprint was made in Topas grade 8007 in order to be able to compare the release of stamps coated with other anti-sticking coatings with the release from stamps coated with the C₄F₈ based coating.

F₁₇TCS based coating

A batch of flat stamps coated with F₁₇TCS were fabricated and the same set of experiments was made as with the C₄F₈ coated stamps, but no experiments involving ZnSt. No adhesion between stamp and polymer was observed when using a F₁₇TCS coated stamp, furthermore
the separation was considerably easier, than for a C₄F₈ coated stamp imprinted in Topas grade 8007. After the first two imprints the stamps were reused without cleaning.

**F₁₃TCS based coating**

At the end of the project a single set of experiments were made, using the homebuilt anti-sticking coating chamber to deposit a F₁₃TCS based coating. A total of four imprints were made using two stamps, one stamp was used a single time and the other was used three times. The separation of the stamps were rather difficult and when reused three times, adhesion of polymer to the stamp was observed. These initial imprints demonstrates the ability to imprint into Topas grade 5013, and when the coating process has been fully optimized the durability of the F₁₃TCS based coating will increase. In Fig. 3.11 the behavior of a drop of water on the surface of a coated and an uncoated stamp is shown.

The entire set of experiments are summarized in Table 3.1. It has to be mentioned that some of the stamps coated with a F₁₇TCS based coating were used several times after these
CHAPTER 3. SURFACE COATINGS FOR NANOIMPRINT

(a) The contact angles of the stamps with regards to a drop of deionized water. It was not possible to measure the contact angle on all stamps after imprint, as the topas had stuck to the stamp.

(b) The contact angles of topas with regards to a drop of deionized water.

Figure 3.12: Contact angles of stamp and Topas before and after imprint. The stamps are coated with a C₄F₈ based coating.

experiments ended, e.g. up to +50 imprints in various Topas grades are recorded.

Surface roughness and contact angle

The contact angle of the coated stamps have been measured with a drop of deionized water after coating for the C₄F₈ and F₁₇TCS based coatings and average values are found to \( \delta(C₄F₈) = 116^\circ \) and \( \delta(F₁₇TCS) = 113^\circ \). The contact angle is measured again after one imprint and for the C₄F₈ based coating it has increased to between 125° and 127°, see Fig. 3.12(a). For the F₁₇TCS based coating no change in contact angle is observed. The contact angle of the surface of Topas grade 8007 and 5013, is measured before and after being imprinted with a C₄F₈ coated stamp, and for both grades an increase in contact angle is observed, see Fig. 3.12(b), this indicate a transfer of material from the anti-sticking coating to the polymer surface. It is observed that the contact angle of stamps coated with a F₁₇TCS based coating does not experience significant changes in contact angle when imprinted many times in Topas. The contact angle of stamps coated with a F₁₃TCS based coating has been measured to \( \delta(F₁₇TCS) = 111^\circ \) after coating. The surface roughness was measured by Atomic Force Microscopy (AFM), using a Dimension 3100 AFM with a RTESP7 tip. The surface roughness is compared to the contact angle for the three investigated anti-sticking coatings. The surface roughness and contact angle are measured after coating, after one imprint and after many imprints. It was only possible to measure the surface roughness after many imprint for the F₁₇TCS coated stamps, as the C₄F₈ based coating is not durable enough to make many imprints. The measurements are
### C₄F₈ coatings deposited by plasma deposition

<table>
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<tr>
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<th>Contact angle</th>
<th>Stamp</th>
<th>Substrate</th>
<th>Imprint</th>
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<tbody>
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<td></td>
<td></td>
<td>δₜₜ</td>
<td>stdv [°]</td>
<td>δₜₜ</td>
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<td>Method A</td>
<td>116.0</td>
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<td>Method A</td>
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<td>± 0.94</td>
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<td>Method A</td>
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### F₁₇ coatings deposited by vapor phase deposition

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### F₁₃ coatings deposited by vapor phase deposition

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<th>Substrate</th>
<th>Imprint</th>
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<tbody>
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<td></td>
<td></td>
<td>δₜₜ</td>
<td>stdv [°]</td>
<td>δₜₜ</td>
</tr>
<tr>
<td>FOTS 01</td>
<td>Method B</td>
<td>110.7</td>
<td>± 0.25</td>
<td></td>
</tr>
<tr>
<td>FOTS 02</td>
<td>Method B</td>
<td>110.7</td>
<td>± 0.25</td>
<td></td>
</tr>
<tr>
<td>FOTS 03</td>
<td>Method B</td>
<td>110.7</td>
<td>± 0.25</td>
<td></td>
</tr>
<tr>
<td>FOTS 04</td>
<td>Method B</td>
<td>110.7</td>
<td>± 0.25</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.1: List of imprints made during the investigation of different anti-sticking coatings. NA indicates that it was impossible to make a measurement due to adhesion problems between polymer and stamp, a blank field indicates that it was possible to make a measurement, but none was made. *) the contact angle has not been measured due to lack of time for experimental work.
CHAPTER 3. SURFACE COATINGS FOR NANOIMPRINT

<table>
<thead>
<tr>
<th></th>
<th>0 imprints</th>
<th>1 imprint</th>
<th>Many imprints</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\delta$ [$^\circ$]</td>
<td>$R_a$ [nm]</td>
<td>$\delta$ [$^\circ$]</td>
</tr>
<tr>
<td>Pure silicon</td>
<td>73</td>
<td>0.0868</td>
<td>$\div$</td>
</tr>
<tr>
<td>$C_4F_8$</td>
<td>110</td>
<td>0.254</td>
<td>129</td>
</tr>
<tr>
<td>MVD</td>
<td>112</td>
<td>0.219</td>
<td>114</td>
</tr>
<tr>
<td>VPD</td>
<td>111</td>
<td>0.295</td>
<td>*)</td>
</tr>
</tbody>
</table>

Table 3.2: Measured contact angle ($\delta$) and surface roughness ($R_a$) of silicon stamps without any anti-sticking coating, stamps coated with fluorocarbon from a $C_4F_8$ plasma and stamps with vapor phase deposited anti-sticking coatings. The silicon and plasma deposited, $C_4F_8$, anti-sticking coating are only imprinted into Topas grade 8007, whereas the vapor phase deposited anti-sticking coating is imprinted into all three Topas grades. The contact angle is measured using method B, and $\div$ indicates that it was impossible to make a measurement, due to adhesion between stamp and polymer. *) the contact angle has not been measured due to lack of time for experimental work.

summarized in Table 3.2. The surface roughness of a $C_4F_8$ coated stamp has increased about an order of magnitude after a single imprint, and when reused the the anti-sticking coating usually fails. The increase in surface roughness indicates a fakir effect, which may explain the increase in contact angle after a single imprint. The surface roughness of a $F_{17}$CST coated stamp does not change significantly after a single imprint, and after many consecutive imprints (+30) the surface roughness has only increased by a factor of three.

It has been experimentally shown that a stamp coated with a $C_4F_8$ based coating is able to imprint in Topas grade 9506 and 8007, without adhesion problems. Stamps coated with a $F_{17}$TCS based anti-sticking coating are able to imprint Topas grade 9506, 8007, 5013 and 6013 without adhesion problems. Furthermore the durability of the $F_{17}$TCS based coating is much better than for a $C_4F_8$ based coating.

3.9 Conclusion

These experiments have shown the limitations of a $C_4F_8$ based coating, with regards to durability and which Topas grades it is possible to imprints.

A commercially available $F_{17}$TCS coating has been tested and has shown excellent performance in terms of stability and durability. Furthermore it allows for successful imprints into more Topas grades than the $C_4F_8$ coating, thus allowing for the fabrication of microsystems in high $T_g$ Topas grades.

Initial test of an in-house fabricated $F_{13}$TCS anti-sticking coating has been made, and it has been shown that it is possible to imprint into Topas grade 5013. The coating is not yet as good as the commercially available coating from Applied Microstructures, but its ability to imprint into Topas grade 5013, and the good performance of coatings based on similar technology, makes it a very promising tool.
Chapter 4

Laser and waveguide theory

In this chapter the basic laser theory will be presented in Sec. 4.1, the optical properties of Rhodamine 6G in Sec. 4.2, and a Brief introduction to waveguides, the cutoff conditions and the loss mechanism in waveguides will be presented in Sec. 4.3.

4.1 Laser Theory

The focus of this project has been on implementing the technology for making NIL in Topas and to integrate a light source, here a microfluidic dye laser, with another optical element. Therefore very little focus has been given to the laser cavity itself, and as a consequence only a brief introduction to laser physic is presented.

4.1.1 Basic laser theory

In order to understand the operation of the laser, we need to understand the interaction between light and matter. The interaction is governed by two phenomonons, the photon and the energy levels of atoms (or matter). During absorption and emission of light the energy of the atom must change a finite amount, $\Delta E$, which is related to the wavelength of the photon by

$$\Delta E = \frac{hc}{\lambda} = hv$$

(4.1)

where $h$ is Planks constant, $c$ is the speed of light, $\lambda$ is the wavelength of the photon and $v$ is the corresponding frequency of the photon. The interaction between light and matter, was described by Einstein in 1916 [52], where he proposed three types of interactions, see Fig. 4.1. The interactions are describe by a system which has two energy levels. The ground state, $E_0$, and the first excited state, $E_1$. The energy difference between the ground state and the first excited state is $\Delta E = E_0 - E_1$. All states above the ground state are called excited states. If an incoming photon has an energy corresponding to $\Delta E$ it may be absorbed by the matter, this will excite an electron to the first excited state, see Fig. 4.1 a). The incoming photon must have an energy that corresponds to the difference between the different states of the atom, i.e. a photon with energy $\frac{\Delta E}{2}$ will not be absorbed, as no state is present at this energy. The transition from the ground state to the first excited state is called stimulated absorption. The
excited electron will, after a short time, decay to the ground state, while emitting a photon of energy $\Delta E$, this process is called spontaneous emission, and is shown in Fig. 4.1 b). The third interaction, which is the most important in the context of lasers, involves an excited electron in the first excited state, and an incoming photon with energy $\Delta E$. When the incoming electron interacts with the atom, the electron in the excited state will decay while emitting a photon identical to the incoming photon. This is shown in Fig. 4.1 c) and is called stimulated emission. The main difference between spontaneous and stimulated emission is that the photons emitted by spontaneous emission has a random phase, polarization and direction, whereas the photon emitted by stimulated emission is identical to the incoming photon with respect to phase, polarization and direction. It is this amplification of a light signal, passing through a medium, that is exploited in lasers. The three types of interactions are controlled by the rate equations. The important feature of these rate equations is that they are proportional to the number of electrons in each state, i.e. the rate of stimulated absorption is proportional to the number of electrons in the ground state while the rate of stimulated emission is proportional to the number of excited electrons in the first excited state. Both processes are proportional to the available number of incoming photons. In order to obtain amplification, a population inversion must be achieved. Population inversion is the excitation of the large part of the electrons in the ground state, such that an incoming photon has a high probability to interact in stimulated emission.
4.1.2 The laser cavity

The laser cavity is usually made of two carefully aligned curved or parallel reflecting mirrors. The function of these mirrors is to reflect photons with the desired properties back into the laser medium for amplification, thus increasing the number of this type of photons by stimulated emission. One of the simplest laser cavities is the Fabry-Perot resonator, which is made of two parallel mirrors with reflectance $R_1$ and $R_2$ respectively and separated by a distance $L$. The Fabry-Perot cavity is transparent and the transfer function through the cavity is given by the Airy function [53]

$$T = \frac{1}{1 + f \sin^2(\frac{\zeta}{2})}$$

(4.2)

here $f = \frac{4v^2}{(1-r^2)^2}$ and $v^2 = \sqrt{R_1 R_2}$. The phase difference between successive reflected beams is $\zeta = \frac{4\pi mL \cos(\theta)}{\lambda}$. Here $\theta = 0$, for two completely parallel mirrors, $m$ is the mode number. The transfer function may be written as

$$T = \frac{(1 - \sqrt{R_1 R_2})^2}{(1 - \sqrt{R_1 R_2})^2 + 4 \sqrt{R_1 R_2} \sin^2\left(\frac{2\pi - mL}{\lambda}\right)}$$

(4.3)

In order to achieve a good amplification, the light needs to travel back and forth inside the cavity, thus resonance must be achieved. In order to do so the amplitude of the propagating field must be zero at the mirrors. As the light is perpendicular to the mirrors and the length of the cavity is fixed, the condition for resonance is given by

$$2Ln = m\lambda, m = 1, 2, 3\ldots$$

(4.4)
CHAPTER 4. LASER AND WAVEGUIDE THEORY

here \( n \) is the refractive index of the medium. A consequence of Eq. (4.4) is that only standing waves fulfill conditions for resonance, and are allowed inside the laser cavity.

### 4.1.3 Lasing threshold

In order to achieve lasing in the laser cavity, the gain in the resonator must exceed the losses. In a laser cavity the loss arises from propagation losses in the laser medium and scattering and absorption losses at the mirrors. Usually the propagation loss in the laser medium is small compared to the loss occurring at the mirrors. The requirement that the gain must exceed the losses sets a lower limit on the gain coefficient, \( G \), below this limit lasing does not occur. Considering the Fabry-Perot cavity from the previous section the gain coefficient is defined as

\[
G = \frac{I(2L)}{I(0)} = R_1 R_2 \exp(2L \sigma (N_2 - N_1))
\]  

(4.5)

here \( I(0) \) is the initial photon flux and \( I(2L) \) is the photon flux after one round trip in the resonator, \( N_2 \) is the number of electrons in the first excited state and \( N_1 \) is the number of electrons in the ground state. For lasing to take place it is required that \( G \geq 1 \), which gives the condition Eq. (4.6)

\[
N_2 \geq N_1 - \frac{1}{2L \sigma} \ln(R_1 R_2)
\]

(4.6)

as \( R_1 R_2 \) is usually smaller than one, \( N_2 \) is required to be larger than \( N_1 \), thus a population inversion must be achieved before lasing takes place.

### 4.2 Rhodamine 6G

A commonly used laser dye for liquid and solid dye laser is Rhodamine. Rhodamine is commercial available and belongs to the Xanthene group of organic dyes. The version of Rhodamine used in this project is Rhodamine 6G (Rh6G). Rh6G is very popular due to its high quantum fluorescence yield and the fact that its absorption maximum is close to 532 nm, which makes it ideal for use together with a commercial available laser: a frequency doubled Nd:YAG laser, which emits laser light at 532 nm. The molecular structure of Rh6G is shown in Fig. 4.3(a) and for liquid lasers it is dissolved in a polar liquid before use, e.g. Ethanol or Ethylene Glycol. The fluorescence, absorption and gain curves for Rh6G are shown in Fig. 4.3(b). The difference between the peak of the absorption and fluorescence curve is called the Stokes shift. For increasing pumping power one will experience a decrease in absorption, and the gain will, due to the Stoke shift, move towards smaller wavelengths as the pump power increase. The band structure of Rhodamine 6G consist of two different states: singlet states and triplet states. Each of these states have a wide range of energy levels, due to rotational and vibrational states of the dye molecules. At room temperature the states are smeared out, and appear as a continuous energy band. The energy diagram for a molecular dye is shown in Fig. 4.2(b), where only the two lowest singlet and the lowest triplet state is shown. In the first step a dye molecule are excited by a pump, and the electrons are excited to a rotational or vibrational state in the first excited singlet state, \( S_1 \), from the ground state, \( S_0 \). The electrons quickly decays to the lowest energy level in \( S_1 \) without emission, as the energy dissipates as heat. From
4.3 Waveguide theory

In this section a brief introduction to waveguides and waveguiding will be given. The cutoff conditions for a planar waveguide will be derived and finally the loss mechanism in waveguides will be presented. This section on waveguide theory is based on textbook material adapted from [56] and [57].
CHAPTER 4. LASER AND WAVEGUIDE THEORY

\[ n_1 \]

\[ n_2 \]

\[ n_3 \]

Figure 4.4: Typical waveguide structure, the guided mode propagate in the core layer in the z-direction. The waveguide is assumed to be infinite in the y-direction, and semi-infinite in the +x and -x direction. It is given that \( n_2 > n_1, n_3 \).

4.3.1 Planar waveguides

A diagram of a three layer planar waveguide is shown in Fig. 4.4. All layers are assumed to be infinite in the y and z direction, and layer one and three are also assumed to be semi-infinite in the x-direction. Optical waves may travel in the second layer in distinct optical modes. A mode is a spatial distribution of energy in one or more dimensions. The mathematical definition of a mode, is an electromagnetic field, which is the solution to Maxwells wave equation

\[ \nabla^2 \tilde{E}(\vec{r}, t) = \left[ \frac{n^2(\tilde{r})}{c^2} \right] \frac{\partial^2 \tilde{E}(\vec{r}, t)}{\partial t^2} \]  \hspace{1cm} (4.7)

here \( \tilde{E} \) is the electric field vector, \( \vec{r} \) is the radius vector, \( n(\tilde{r}) \) is the refractive index and \( c \) is the speed of light. The solution to Eq. (4.7) for monochromatic waves has the form \( \tilde{E}(\vec{r}, t) = \tilde{E}(\vec{r}) \exp(i\omega t) \), where \( \omega \) is the frequency. Inserting the solution into Eq. (4.7) gives

\[ \nabla^2 \tilde{E}(\vec{r}) + k^2 n^2 \tilde{E}(\vec{r}) = 0 \]  \hspace{1cm} (4.8)

where \( k \equiv \frac{\omega}{c} \). If we assume that an uniform wave propagates in the z direction, that is \( \tilde{E}(\vec{r}) = \tilde{E}(x,y) \exp(-i\beta z) \), where \( \beta \) is a propagation constant, we are able to write Eq. (4.8) separately for the three regions, taking into account that the waveguide is infinite in the y-direction.

Layer 1  \[ \frac{\partial^2 \tilde{E}(x,y)}{\partial x^2} + (k^2 n_1^2 - \beta^2) \tilde{E}(x,y) = 0 \]

Layer 2  \[ \frac{\partial^2 \tilde{E}(x,y)}{\partial x^2} + (k^2 n_2^2 - \beta^2) \tilde{E}(x,y) = 0 \]  \hspace{1cm} (4.9)

Layer 3  \[ \frac{\partial^2 \tilde{E}(x,y)}{\partial x^2} + (k^2 n_3^2 - \beta^2) \tilde{E}(x,y) = 0 \]

The solutions to the wave equations are either sinusoidal or exponential functions. This depends on weather \( (k^2 n_i^2 - \beta^2) \), \( i=1,2,3 \) is larger than or smaller than zero. In Fig. 4.5 the possible mode configurations are shown. The frequency, \( \omega \), is considered constant and the mode shape changes as a function of \( \beta \). It is required that \( \tilde{E}(x,y) \) and \( \frac{\partial \tilde{E}(x,y)}{\partial x} \) are continuous at the interfaces between the layers. Furthermore \( n_2 > n_3 > n_1 \). When \( \beta > kn_2 \) the solution to the wave equation must be exponential in all three layers, and the only mode shape that fulfills this and continuity of \( \tilde{E}(x,y) \) and \( \frac{\partial \tilde{E}(x,y)}{\partial x} \) is the one shown in a) in Fig. 4.5. However this solution is not physically possible as the field increases in layer one and three, thus indicating a wave with infinite energy. For \( kn_3 < \beta < kn_2 \), well confined modes are observed, and in b) and c) the zeroth and first order transverse electric (TE) modes are shown. For \( kn_1 < \beta < kn_3 \),
Figure 4.5: Possible mode combinations in a three layer planar waveguide. The solutions to the wave equations are usually sinusoidal or exponential functions. Situation a) refers to where the solution is exponential in all three layers, this is not physically possible, as it indicates infinite energy in the mode. For situation b) and c) the solution is only sinusoidal in the second layer and the modes are guided. Situation d) is called a substrate radiation mode, as the mode is sinusoidal in the second and third layer, which means that the mode continuously will lose energy to the third layer. Situation e) shows an unguided mode, where the solution to the wave equations are sinusoidal in all three layers, and the energy is free to spread out. Adapted from [56]
CHAPTER 4. LASER AND WAVEGUIDE THEORY

the mode will be confined at the interface between layer one and two, but as the mode is not confined by layer three it will oscillate and continuous transfer of energy from layer two to layer three will take place, as a result the mode will be damped out over a short distance, see d). For \( \beta < kn_1 \) no guidance takes place and the solution to the wave equation is oscillating in all three layers and the energy is free to spread out as shown in e).

4.3.2 Cutoff conditions for waveguides

In Fig. 4.4 the typical structure of a slab waveguide is shown. The core of the waveguide, with refractive index \( n_2 \) and thickness \( t_g \), is surrounded by materials with lower refractive indexes, \( n_1 \) and \( n_3 \), such that \( n_2 > n_1, n_3 \). The two surrounding layers are assumed to extend to infinity in the x-direction. For the TE mode Maxwell's wave equation reduces to

\[
\nabla^2 E_y = \frac{n_2^2}{c^2} \frac{\partial^2 E_y}{\partial t^2}, \quad i = 1, 2, 3
\]  

(4.10)

The index \( i \) correspond to the three layers in the waveguide structure. The solution to the wave equation has the form

\[
E_y(x, z, t) = \varepsilon_y(x) \exp(i(\omega t - \beta z))
\]  

(4.11)

As stated in the previous section, solutions to Maxwell's wave equation must have an exponential form in layer one and three, and a sinusoidal form in layer two, in order to guide the light. Therefore the general solution has the form

\[
\varepsilon_y(x) = \begin{cases} 
A_w \exp(-q_w x) & , 0 \leq x \leq \infty \\
B_w \cos(h_w x) + C_w \sin(h_w x) & , -t_g \leq x \leq 0 \\
D_w \exp[p_w(x + t_g)] & , -\infty \leq x \leq -t_g 
\end{cases}
\]  

(4.12)

\( A_w, B_w, C_w, D_w, q_w, h_w \) and \( p_w \) are all constants that can be determined by matching the boundary conditions, which requires that \( \varepsilon \) and \( \mathcal{H}_z = \left( \frac{1}{\omega_0} \right) \frac{\partial \varepsilon}{\partial x} \) is continuous at the interfaces. The permeability of the dielectric material, \( \mu \) and the frequency of the light, \( \omega \) are assumed to be constant, which reduces the second requirement to: \( \frac{\partial \varepsilon}{\partial x} \) must be continuous at the interfaces. By making \( \varepsilon_y \) continuous at both boundaries between the layers and \( \frac{\partial \varepsilon}{\partial x} \) continuous at the boundary between layer one and two, \( \varepsilon_y(x) \) may be expressed as

\[
\varepsilon_y(x) = \begin{cases} 
C' \exp(-q_w x) & , 0 \leq x \leq \infty \\
C' \left[ \cos(h_w x) - \left( \frac{q_w}{h_w} \right) \sin(h_w x) \right] & , -t_g \leq x \leq 0 \\
C' \left[ \cos(h_w t_g) + \left( \frac{q_w}{h_w} \right) \sin(h_w t_g) \right] \exp[p_w(x + t_g)] & , -\infty \leq x \leq -t_g 
\end{cases}
\]  

(4.13)

The constants, \( q_w, h_w \) and \( p_w \) may be found by inserting Eq. (4.13) into Eq. (4.11) by using the resulting expression for \( E_y(x, z, t) \) in Eq. (4.10) for each of the three layers.

\[
\begin{align*}
q_w &= (\beta^2 - n_1^2 k^2)^{\frac{1}{2}} \\
h_w &= (n_3^2 k^2 - \beta^2)^{\frac{1}{2}} \\
p_w &= (\beta^2 - n_3^2 k^2)^{\frac{1}{2}} \\
k_w &= \frac{\omega}{c} = \frac{2\bar{\beta}}{\lambda}
\end{align*}
\]  

(4.14)

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By taking $\frac{\partial \varphi}{\partial x}$ and making it continuous at the boundary between layer two and three, the following requirement on $\beta$ may be derived from Eq. (4.13)

$$\tan(h_w \, t_g) = \frac{p_w + q_w}{h_w \left(1 - \frac{p_w \, q_w}{h_w^2}\right)}$$

(4.15)

by inserting Eq. (4.14) into Eq. (4.15) a set of discrete values for $\beta$ may be found. Each discrete value of $\beta$ corresponds to an allowed mode, with an individual propagation constant $\beta_m$. As described in Sec. 4.3.1 the wave equation needs to be sinusoidal in layer two, and exponential decaying in layer one and three in order to ensure waveguiding, therefore we may impose the following condition on the allowed $\beta_m$ values

$$kn_1, kn_3 < \beta_m < kn_2$$

(4.16)

As we know the requirements on $\beta_m$ and it is possible to derive the conditions for the cutoff conditions for a given mode, here the lowest order mode is of most interest as it denotes the situation where no light is guided, thus the field in layer one and three becomes oscillatory. First the symmetric waveguide is examined, where $n_1 = n_3$, and $\beta$ is given by: $\beta = kn_1 = kn_3$. This may be inserted into Eq. (4.14) which yields the condition for cutoff when inserted in Eq. (4.15)

$$\tan(h_w \, t_g) = 0 \Rightarrow h_w \, t_g = m_s \pi, m_s = 0, 1, 2, \ldots$$

(4.17)

If waveguiding for a given mode must occur, one must have that

$$t_g > \frac{m_s \lambda}{2 \sqrt{(n_2 + n_1)\Delta n}}, \quad m_s = 0, 1, 2, \ldots$$

(4.18)

The cutoff condition in Eq. (4.18) determines which modes that can be supported by a waveguide, for a given wavelength, $\lambda$, thickness of the waveguide, $t_g$ and difference in refractive index between the core and the cladding layer, $\Delta n = n_2 - n_1$. It is interesting that the zeroth order mode, $m_s=0$, does not experience cutoff. A consequence of this is; that in principle any wavelength could be guided for the symmetric waveguide, however for small $\Delta n$ and large $\lambda/t_g$ the guiding will be poor, and large evanescent tails of the zeroth order mode will extend into the substrate. It is possible to find a cutoff condition for the asymmetric waveguide, where $n_3 \gg n_1$, by applying a geometrical argument, which compares it to the symmetrical waveguide. In Fig. 4.6 the two lower order modes for the symmetric and the asymmetric waveguide are shown. The asymmetric waveguide is half as thick as the symmetric waveguide. For a well confined wave, the lower half of the first order mode in the symmetrical waveguide, $m_s = 1$ is comparable to the lower half of the zeroth order mode in the asymmetrical waveguide, $m_s = 0$. By exploiting this similarity and solving Eq. (4.15), as for the symmetric waveguide with a thickness of $2t_g$, one yields the condition for cutoff condition for an asymmetric waveguide.

$$t_g > \frac{(m_s)\lambda}{4 \sqrt{(n_2 + n_3)\Delta n}}, \text{ where } \quad m_s = 2m_a + 1, m_a = 0, 1, 2, \ldots$$

(4.19)

For an symmetric waveguide the lowest order mode will experience cutoff. The cutoff conditions have been derived for TE waves, but it has been shown that the cutoff conditions also holds for TM waves, when $n_2 \approx n_3$ [57].
4.3.3 Example: Cutoff conditions for Topas

The cutoff condition Eq. (4.19) may be used to find the minimum thickness, \( t_g \), for which not even the fundamental mode is guided. Two situations will be investigated. 1) Topas grade 8007 on SiO\(_2\) (\( n=1.46 \)), which corresponds to normal imprint conditions. 2) Topas grade 9506 on a Pyrex glass wafer (\( n=1.50 \)), which is the setup used for bonding. For both situations it will be calculated how thin the Topas layer must be, such that not even the zeroth order mode is guided. The Topas layers in the examples are considered as asymmetric waveguides with air to one side. The wavelength is set to 570 nm as this is the lowest wavelength for which lasing is observed. The refractive index of Topas grade 9506 and 8007 is set to 1.53 [51].

For Topas grade 8007 on SiO\(_2\)

\[
t_g > \frac{(2m + 1)\lambda}{4\sqrt{(n_2 + n_3)\Delta n}} = \frac{570\text{nm}}{4\sqrt{(1.46 + 1.53)0.07}} = 312\text{nm}
\]  \hspace{1cm} (4.20)

For Topas grade 9506 on Pyrex

\[
t_g > \frac{(2m + 1)\lambda}{4\sqrt{(n_2 + n_3)\Delta n}} = \frac{570\text{nm}}{4\sqrt{(1.50 + 1.53)0.03}} = 473\text{nm}
\]  \hspace{1cm} (4.21)

From Eqs. (4.20) and (4.21) it is found that the residual layer after imprint in Topas grade 8007 must not be thicker than 312 nm, and the layer of Topas grade 9506 used for bonding, must not be thicker than 473 nm, if light is not to be guided.

4.3.4 Loss mechanisms in waveguides

The next most important question regarding waveguides, after having determined which modes that propagate, is the loss. The loss in waveguides is usually accounted for by three mecha-
nisms; scattering, absorption and radiation. Scattering usually dominates in glass and dielectric materials, while absorption dominates in semiconductors and other crystalline materials. Radiation loss takes place when waveguides bend in a curve. In this thesis only scattering and radiation loss will be presented.

Scattering losses

Two types of scattering losses are present in optical waveguides. Volume scattering and surface scattering. Volume scattering is caused by imperfections in the waveguide, such as voids, contaminated atoms and crystalline defects. Volume scattering is for most waveguides negligible when compared to surface scattering. Surface scattering is caused by scattering events at the surface of the waveguide. The surface scattering loss can be high even for very smooth waveguides, as the light interacts heavily with the surface of the waveguide. The loss in the waveguide may be described by the exponential attenuation coefficient, $\alpha_s$, and the intensity for a wave propagating in the $z$-direction is usually describe by

$$I(z) = I_0 \exp(-\alpha z) \quad (4.22)$$

here $I_0$ is the initial intensity and $I(z)$ is the intensity in the distance $z$. The scattering is related to the surface roughness and therefore a smoother surface will reduce scattering loss. An expression for calculating the exponential attenuation coefficient has been made [56]

$$\alpha_s = A^2 \left\{ \frac{\cos^3(\theta'_m)}{2 \sin(\theta'_m)} \right\} \left\{ \frac{1}{t_g + 1/p + 1/q} \right\} \quad (4.23)$$

where $t_g$ is the thickness of the waveguide, $\theta'_m$ is the angle of incidence, if the light is considered using a ray-optic approach, $p$ and $q$ are the attenuation coefficients in the confining layers, see Sec. 4.3.2, and $A$ is given by

$$A = \frac{4\pi}{\lambda_2} \sqrt{\sigma_{12}^2 + \sigma_{23}^2} \quad (4.24)$$

where $\lambda_2$ is the wavelength of the light confined in the waveguide, and $\sigma_{12}^2$ and $\sigma_{23}^2$ are the variance in the surface roughness. Remembering that $\sigma$ of a given variable $x$, is defined as $\sigma^2 = S[x^2] - S^2[x]$, where $S$ is the mean value. Eq. (4.23) is based on the Rayleigh criterion, which states that: if the incoming beam at the surface has the power $P_i$, then the specularly reflected beam has the power

$$P_t = P_i \exp \left[ - \left( \frac{4\pi \sigma}{\lambda_2 \cos(\theta'_m)} \right)^2 \right] \quad (4.25)$$

From Eq. (4.23) it is seen that the scattering loss is increased for well confined modes, as they are more affected by the surface roughness than modes with a large evanescence tail. This is physically explained by the penetration into the confining layers of a mode. If the penetration is large, the effect of the surface roughness will be averaged out. The factor $\cos^3(\theta'_m)/\sin(\theta'_m)$ accounts for the greater loss for high order modes, for which $\theta'_m$ is small, as they have more reflections at the surface per unit length of the waveguide.
Chapter 4. Laser and Waveguide Theory

Radiation scattering

Radiation loss occurs when waveguides bend, and the reason for this, is the distortion the optical field experience, when it travels through a bend. In Fig. 4.7, a diagram for calculating the radiation loss by the velocity approach is shown. The diagram shows a bend in a waveguide, with radius $R$. A wave travelling through the bend is shown and the velocity of the phase front must be proportional to the distance from the center of curvature, i.e. that part of the phase front furthest away from the center of curvature, must have a higher velocity in order to keep up with the wavefront. As the evanescent tail travel in the confining layer, with refractive index, $n_1$, it can not travel faster than unguided light in the confining layer. There will be a point $(R + X_r)$ where the velocity of the phase front will have to travel faster than the unguided light in order to keep up with the phase front. When the photons can not keep up with the phase front they split away and radiate into the surrounding layers. As $\frac{d\theta}{dt}$ must be the same for all waves along the phase front, two equalities may be formulated

$$(R + X_r) \frac{d\theta}{dt} = \frac{\omega}{\beta_0} \quad \text{and} \quad R \frac{d\theta}{dt} = \frac{\omega}{\beta_z} \quad (4.26)$$

where $\beta_0$ is the propagation constant of unguided light in the medium surrounding the waveguide, $\beta_z$ is the propagation constant of light in the waveguide. By combining the two equalities one gets an expression for $X_r$

$$X_r = \frac{\beta_z - \beta_0}{\beta_0} R \quad (4.27)$$

In order to estimate how far a photon must travel in order to be considered removed from the guided mode, a simple analogy may be set up. Considerer an abruptly terminated waveguide, with a near beam field width, $a$, as the one shown in Fig. 4.8. It has been shown that light emitted into a medium from such a waveguide remains collimated within the waveguide
Figure 4.8: Spread of light from a truncated waveguide. The emitted light remains collimated within the waveguide thickness, \( a \) over a distance \( Z_c \)

thickness over a length, \( Z_c \), which is given by

\[
Z_c = \frac{a}{\phi} = \frac{a^2}{2\lambda_1} \tag{4.28}
\]

where \( \lambda_1 \) is the wavelength in the medium surrounding the waveguide and \( \phi \) is the far field angle, see Fig. 4.8 for definition. The exponential attenuation coefficient is related to the power lost per unit length of the waveguide and is given as

\[
\alpha = \frac{-1}{P(z)} \frac{dP(z)}{dz} \approx \frac{1}{P_l Z_c} \tag{4.29}
\]

here \( P(z) \) is the power transmitted, thus we may define \( P_l \) as the power in the evanescence tail beyond \( X_r \), i.e. the amount of power lost by radiation within a length \( Z_c \). \( P_l \) is defined as the total amount of power transmitted by the waveguide. \( P_l \) can be found by integrating over the electric field, for radii greater than \( R + X_r \), \( P_l \) is found by integrating over the entire wave. The exponential attenuation coefficient becomes

\[
\alpha = \frac{\beta \cos^2 \left( \frac{ha}{2} \right) \exp \left( -\frac{2 \beta}{\beta_0} R \right) 2\lambda_1 \exp \left( \frac{a}{\beta} \right)}{\left[ \frac{a}{2} + \frac{a h}{\pi} \sin(ha) + q \cos^2 \left( \frac{ha}{2} \right) \right] a^2} \tag{4.30}
\]

which may be simplified to fit the simple form

\[
\alpha = C_1 \exp(-C_2 R) \tag{4.31}
\]

where \( C_1 \) and \( C_2 \) are constant that depend on the size and dimensions of the waveguide, and on the shape of the optical mode. The important feature of Eq. (4.31) is that the radiation loss depends exponentially on the radii of curvature, \( R \).
CHAPTER 4. LASER AND WAVEGUIDE THEORY
Chapter 5

Topas - a cyclic-olefin-copolymer

In this chapter a brief summary of the Topas synthesis and some details about the structure of Topas will be presented. Furthermore the material properties of Topas will be presented and compared to other polymers commonly used for LOC applications.

Polymer, which means many parts, is a material that is constructed of smaller molecules of the same substance, that form large molecules, usually long chains. The smaller molecules are referred to as monomers. When two or more different monomers are arranged in a long chain they are referred to as copolymers. The different monomers in a copolymer can be arranged in a random or in a repeated way. These polymer or copolymer chains form the bulk of the polymer material, and the interaction between these polymer chains determines the macroscopic properties of the material. The type of thermoplastic used in this thesis is a cyclic-olefin-copolymer (COC) sold under the commercial name Topas. Topas is a acronym and stands for Thermoplastic Olefinic Polymer of Amorphous Structure. The term, cyclic-olefin-copolymer, simply means that the polymer is made up of different kinds of monomers, hence copolymer, and that one of these monomers is a ring shaped monomer, hence cyclic. The term olefin relates to the fact that one of the monomers is a hydrocarbon, which has a double bond between two carbon atoms, these double bonds are sometimes called a olefinic linkage, hence the name olefin.

Topas contains two monomers, Norbornene and Ethylene, see Fig. 5.1(b). Norbornene is a large ring shaped molecule, whereas Ethylene is a small molecule that, when put one after another, forms a long chain. Topas and other COCs are interesting materials due to some attractive material properties. These properties include low moisture uptake, high optical transmission due to a glass like transparency and good resistance to polar solvents. For Topas it is possible to tune the glass transition temperature, $T_g$, from 65°C up to 170°C by varying the content of the two monomers [6]. The development of Topas was initiated in 1990 by Ticona and in 1996 a pilot plant began the first large scale production of Topas.

5.1 Synthesis of Topas

Topas is polymerized in a two step process, which is shown in Fig. 5.1(a). Ethylene and Cyclopentadiene are used as raw materials, and the first step in the process involves the polymer-
50

CHAPTER 5. TOPAS - A CYCLIC-OLEFIN-COPOLYMER

(a) The synthesis of Topas. Ethylene and cyclopentadiene are used as raw materials. In an intermediate step the Cyclopentadiene is transformed into Norbornene and then norbornene and Ethylene is chain polymerized by the aid of a Metalloocene catalyst, thus forming the finished Topas molecule. Adapted from [58]

(b) The structure of Topas. The polymer consists of Norbornene, to the left, and Ethylene, to the right. The m and n shows the ratio between the two monomers for a given composition. The ratio also determines the glass transition temperature, $T_g$. Adapted from [6]

Figure 5.1: The synthesis and molecular structure of Topas.

...
Figure 5.2: Nuclear Magnetic Resonance (NMR) spectra of Cyclic-olefin-copolymers (Topas) with norbornene content of a) 36.1, b) 58.1, c) 63.0 and d) 79.0 mol%. The peaks indicate which bonds are present in the different samples of Topas. For increasing amounts of Norbornene, the amount of Ethylene to Ethylene bonds are decreasing, whereas the amount of Norbornene to Norbornene bonds are increasing. See the text for more details. (Adapted from [59])

spectras that are depicted in Fig. 5.2 b)-d) shows a different architecture of the polymer chain. The large peak for Ethylene-Ethylene bonds at 30 ppm is considerably lower than for Fig. 5.2 a). The structure of the three peaks that depicts the bonding of the Norbornene monomers around 48 ppm has significantly changed. The first peak to the left that indicates Norbornene to Norbornene bonds has increased, and the third peak from the left that depicts a Norbornene monomer that bonds to at least one Ethylene monomer is partially affected. The Peak that indicates a Norbornene monomer bonded to at least two Ethylene monomers is almost depleted, when the Norbornene content is higher than 50 mol%. The composition of the molecular structure of the Topas may be separated into two regimes. 1) A low Norbornene regime, where the Norbornene monomers are mainly incorporated in blocks with Ethylene monomers. The resulting structure is alternating Norbornene and Ethylene units and longer chains of Ethylene monomers. 2) A high Norbornene regime, where blocks of Norbornene is incorporated with alternating blocks of Norbornene and Ethylene. These results have been confirmed by Delfolie et al. [60] and Shin et al. [61].

The wt% and mol% of Norbornene in different Topas grades are summarized in Table 5.1. The low $T_g$ grades of Topas, 9506 and 8007, belong to the low Norbornene content regime, and the high $T_g$ grades, 5013, 6013, 6015 and 6017, belong to the high Norbornene content regime.
CHAPTER 5. TOPAS - A CYCLIC-OLEFIN-COPOLYMER

<table>
<thead>
<tr>
<th>Grade</th>
<th>9506</th>
<th>8007</th>
<th>5013</th>
<th>6013</th>
<th>6015</th>
<th>6017</th>
</tr>
</thead>
<tbody>
<tr>
<td>wt%</td>
<td>63</td>
<td>66</td>
<td>78</td>
<td>79</td>
<td>83</td>
<td>86</td>
</tr>
<tr>
<td>mol%</td>
<td>26</td>
<td>30</td>
<td>50</td>
<td>50</td>
<td>54</td>
<td>58</td>
</tr>
</tbody>
</table>

Table 5.1: The wt% and the mol% of Norbornene in Topas. The value have been read of graphs from Ticona [6]. The table has been made in order to link the Topas grade with their respective wt% and mol%, as Ticona and many publications frequently refer to Topas grades by either their name, their wt% or mol% content of Norbornene.

A paper on the influence of the Norbornene content in Topas during Uniaxial elongation flow have been presented by Maiti et al. [62]. They reports that COCs with a Norbornene content below 30 mol% has two glass transition temperatures when elongated. This effect is caused by areas of the polymer having many entangled Norbornene monomers, and other areas having very few entangled Norbornene Monomers, each of these areas has a characteristic $T_g$, which is determined by the entanglement of the Norbornene monomers. When the Norbornene content is increased, enough Norbornene monomers are present through out the COC, in order to ensure a homogeneous entanglement, thus it has only one glass transition temperature. If this has any influence on the imprint process is still unknown.

5.2 Material properties

Topas was originally developed in order to improve some of the limitations associated with PMMA and similar polymers: relative high optical loss, limited resistance to dry etches and chemicals, and at the same time keep the desired properties. As a result Topas has a lower optical loss, higher chemical resistance to acids and polar organic solvents. Furthermore Topas has a higher moisture barrier and is resistant towards dry etch.

PMMA is a thermoplastic polymer which can be patterned with NIL, with laser ablation using a CO$_2$ laser or with electron beam lithography. SU-8 is a negative tone epoxy based resist developed by IBM [63] and can be patterned with UV-Lithography or electron beam lithography. The fabrication methods for SU-8 and PMMA are somewhat different than the NIL method used in this thesis, but due to the frequent use of SU-8 [11,19] and PMMA [64–67] in LOC applications a comparison is in place. For SU-8 the comparison is made with crosslinked SU-8, as it is the final state of SU-8 after UV-lithography and development. The material properties are listed in Table 5.2, and it is seen that Topas has a low optical loss, and is resistant to acids, bases and polar organic solvents.

Data for the bulk viscosity of Topas grades at elevated temperatures are not available from the supplier, and as a part of this project, the bulk viscosity of topas 9506 and 5013 has been measured. The viscosity was measured as a function of shear rate, using a TA Instruments AR 2000 rheometer, with a 25 mm parallel plate geometry. Prior to the measurements a 1 mm thick plates of topas with a diameter of 25 mm were molded from Topas pellets. The values for the zero shear rate viscosities were found by fitting a Carreau model to the data point. The zero shear rate viscosities for Topas grade 9506, 8007 and 5013 at elevated temperatures are presented in Table 5.3.
<table>
<thead>
<tr>
<th></th>
<th>Topas</th>
<th>PMMA</th>
<th>SU-8</th>
</tr>
</thead>
<tbody>
<tr>
<td>(n)</td>
<td>1.53</td>
<td>1.49</td>
<td>1.59</td>
</tr>
<tr>
<td>(T_g[^\circ C])</td>
<td>65-170</td>
<td>95-105</td>
<td>(\geq 200)</td>
</tr>
<tr>
<td>water abs. [%]</td>
<td>0.03</td>
<td>(&lt; 0.01)</td>
<td>N/A</td>
</tr>
<tr>
<td>loss [dB/cm]</td>
<td>0.5 [820 nm]</td>
<td>2.0 [820 nm]</td>
<td>6.0 [850 nm]</td>
</tr>
<tr>
<td>bio compatible</td>
<td>yes</td>
<td>yes</td>
<td>yes</td>
</tr>
<tr>
<td>dry etch resistance</td>
<td>good</td>
<td>poor</td>
<td>good</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>chemical resistance</th>
<th>Topas</th>
<th>PMMA</th>
<th>SU-8</th>
</tr>
</thead>
<tbody>
<tr>
<td>alcohols</td>
<td>yes</td>
<td>poor</td>
<td>yes</td>
</tr>
<tr>
<td>acids</td>
<td>yes</td>
<td>no</td>
<td>yes</td>
</tr>
<tr>
<td>bases</td>
<td>yes</td>
<td>no</td>
<td>yes</td>
</tr>
<tr>
<td>polar org. solvents</td>
<td>yes</td>
<td>no</td>
<td>yes</td>
</tr>
<tr>
<td>nonpolar org. solvents</td>
<td>no</td>
<td>no</td>
<td>yes</td>
</tr>
</tbody>
</table>

Table 5.2: Comparison of physical and chemical properties for Topas, PMMA and crosslinked SU-8. N/A indicates that no data are available. The data are adapted from [5,6,68–70]

<table>
<thead>
<tr>
<th>Topas grade 9506 (T_g = 65[^\circ C])</th>
<th>Topas grade 8007 (T_g = 75[^\circ C])</th>
<th>Topas grade 5013 (T_g = 135[^\circ C])</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature °C</td>
<td>(\eta_0) Pa s</td>
<td>Temperature °C</td>
</tr>
<tr>
<td>130</td>
<td>790000</td>
<td>170</td>
</tr>
<tr>
<td>145</td>
<td>169000</td>
<td>180</td>
</tr>
</tbody>
</table>

Table 5.3: Glass transition temperature and zero shear rate viscosities for Topas grade 9506, 8007 and 5013, respectively. The viscosity was measured as a function of shear rate using a TA Instruments AR 2000 rheometer, with a 25 mm parallel plate geometry. The values for the zero shear rate viscosities were found by fitting a Carreau model to the data points. Data for Topas grade 8007 are adapted from [71]
CHAPTER 5. TOPAS - A CYCLIC-OLEFIN-COPOLYMER
Chapter 6

Design and Fabrication

This chapter will describe the design and fabrication of the devices made in this project. The design of the devices and the individual optical elements is presented in Sec. 6.1. The design of the LOC device is presented in Sec. 6.2, and the lasers for comparison of conventional and Fresnel lenses are presented in Sec. 6.3. In Sec. 6.4 the fabrication process is presented, including the changes and improvements that have been made during this project. Finally the fabrication issues will be presented in Sec. 6.5.

6.1 Design considerations

The scope of this project is to fabricate a device with integrated optical elements by nanoimprint lithography. Given the technology base of the group, it is obvious that the light source is the microfluidic dye laser. Initially the laser was to be integrated with a flowcytometer [11], which had previously been fabricated and tested at MIC in SU-8. The flowcytometer contained a non-spherical lens for focusing the light in the middle of the flow channel, and this lens had been developed empirically by a number of iterations and no tool for designing such a lens from the bottom, was available at MIC. This would make the migration of the design from SU-8 (n=1.59) to Topas (n=1.53) very difficult, as the refractive index is somewhat different. It was estimated that the development of a similar lens in Topas would be too time consuming, and therefore it was decided to integrate an absorption detection cell instead. However, the requirement for a focused light and an inlet structure with three inlets was maintained, thus only the central element of the flowcytometer was discarded. This would pave the way for a future integration of a flowcytometer with the microfluidic dye laser.

6.1.1 Absorption detection cell

A cell for absorption measurements can be fabricated in two ways. The light path can be perpendicular to microfluidic channel or the light path can be parallel with the microfluidic channel. The second option has the advantage that the optical path through the sample liquid is longer, thus it should be possible to achieve a higher sensitivity. This is also known from Lambert-Beers law which states

\[ A = \epsilon c b \]   

(6.1)
CHAPTER 6. DESIGN AND FABRICATION

Figure 6.1: Two realizations of an absorbance detection cell. left: The light path is perpendicular to the microfluidic channel, and the optical interaction length is comparable to the width of the channel. right: The light path is parallel to the microfluidic channel, and the optical interaction length is much longer than the width of the channel, thus increasing the measured signal.

Figure 6.2: Optical image of the absorption detection cell, some lengths are added to the image, and the full summary on design parameters can be found in Table 6.1.

where, \( A \) is the absorbance, \( \epsilon \) is the molar absorptivity, \( b \) the length of the optical path and \( c \) is the concentration. \( A \) is usually measured by

\[
A = \log \left( \frac{P_0}{P} \right)
\]  

(6.2)

where \( P_0 \) is the radiant power of the incoming beam and \( P \) is the radiant power of the outgoing beam. It was decided to fabricate an absorption detection cell, where the light path is parallel to the microfluidic channel, see Fig. 6.2. The design is a bit more complex than what has previously been made at MIC by K. B. Mogensen et al. [72, 73], as a small lens has been added to focus the light into the waveguide after the detection cell, thus collecting as much light as possible in order to get better results. The incoming waveguide has been tapered in order to ensure a more collimated light beam inside the detection cell, the tapered waveguide design is adapted from [74]. The design parameters of the absorption cell are summarized in Table 6.1.

6.1.2 Microfluidic network

The microfluidics in this project are pressure driven, and the flow profile is the well-known parabolic shape. It has been found that a constant pressure drop, \( \Delta p \), along the channel, will
<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Channel width</td>
<td>90 μm</td>
</tr>
<tr>
<td>Lens height</td>
<td>170 μm</td>
</tr>
<tr>
<td>Channel height</td>
<td>10 μm</td>
</tr>
<tr>
<td>Lens radii of curvature</td>
<td>1500 μm</td>
</tr>
<tr>
<td>Channel length</td>
<td>260 μm</td>
</tr>
<tr>
<td>Taper angle</td>
<td>6.6°</td>
</tr>
<tr>
<td>Lens to waveguide distance</td>
<td>325 μm</td>
</tr>
<tr>
<td>Taper length</td>
<td>130 μm</td>
</tr>
<tr>
<td>Incoming waveguide to u-cell</td>
<td>30 μm</td>
</tr>
<tr>
<td>Distance from u-cell to lens</td>
<td>30 μm</td>
</tr>
</tbody>
</table>

Table 6.1: Design parameters of the absorption detection cell. The absorption cell is shown in Fig. 6.2

result in a constant flow rate, $Q$. This can be summarized in the the Hagen-Poiseuille law

$$\Delta p = R_{\text{hyd}} Q$$

(6.3)

which is an analogous to Ohm’s law, $\Delta V = R \times I$, relating the electrical current, $I$, through a wire with the electric resistance $R$ and the electrical potential drop $\Delta V$ along the wire. The factor $R_{\text{hyd}}$ is known as the hydraulic resistance of the channel. The Hagen-Poiseuille law is valid for low values of Reynolds number

$$Re = \frac{\rho V_0 L_0}{\eta}$$

(6.4)

where $\rho$ is the density of the liquid, $V_0$ is the velocity scale of the system, $L_0$ is the length scale of the system and $\eta$ is the viscosity of the liquid in the channel. In practice $V_0$ is the characteristic velocity of the liquid in the channel, and $L_0$ is the smallest dimension of the channel, typical the height. When the Reynolds number is low, $Re \leq 1$, Eq. (6.3) is valid and one can use Kirchhoffs law to predict the flow of the liquid in the channel. In this project the sample liquid is pumped through the device by hand, and therefore it is difficult to estimate if $Re \leq 1$. If one takes the dimensions of the channels into consideration, it is possible to pump 0.5 ml of liquid through the channels per hour and still have a Reynolds number, which is less than one. During the experiments the use of sample liquid never exceeded 0.5 ml per hour, and it is therefore fair to use Kirchhoffs law to predict the flow in the microchannels. A view of the equivalent circuit for the microfluidic network is seen in Fig. 6.3. In order to ensure that the liquid prefers to flow towards the outlet, the flow resistance in the three inlets, should be larger than the flow resistance in the channel from the mixer and to the outlet. The hydraulic resistance for a rectangular channel of length $L$, height, $h$ and width, $w$ is given by [31]

$$R_{\text{hyd}} = \frac{12\eta L}{1 - 0.63(h/w)} \frac{1}{h^3 w}$$

(6.5)

where $\eta$ is the viscosity of the liquid. As the height of the channel is fixed for all channels, the variable parameters are the channel width, $w$ and the channel length, $L$. In general the hydraulic resistance is increased by varying the channel length, and in order to maintain a small chip, the channels are given a meander shape. In Fig. 6.3 the microfluidic network and the equivalent diagram are seen. The three inlets are given a meander shape in order to increase the length and thereby increasing the hydraulic resistance, and the outlet channel has
CHAPTER 6. DESIGN AND FABRICATION

Figure 6.3: The Equivalent diagram and the actual microfluidic network. left: Equivalent diagram of the network. The flow directions are shown and the hydraulic resistance is symbolized by normal resistors. In this case, R₁=R₃, as these two inlets are similar. right: The actual microfluidic network. The three inlets are shown to the left and the outlet is going round the absorbance cell and upwards.

been widened in order to decrease the hydraulic resistance. Therefore the hydraulic resistance is twice as high in the inlets, than in the outlet. The fluidic network may be separated into three parts. The inlets, the absorbance detection cell, and the outlet. The channel height is 10 μm for all three parts, and the dimensions of the absorption detection cell are listed in Sec. 6.1.1. The inlets are 90 μm wide and 7.5 mm long. The middle channel is 1200 μm longer than the two other inlets, in order to make room for the meander shape. The outlet is initially 90 μm wide but over a 500 μm distance the width is increased to 180 μm. When the width has increased to 180 μm, the remaining length of the outlet is 5.7 mm. The inlet circles are 2.5 mm in diameter.

6.1.3 Micro fluidic dye laser

The microfluidic dye laser which is fabricated in this project is directly adapted from Søren Balslev [75] and Daniel Nilsson [76]. This laser design has been realized in SU-8 by Søren Balslev using UV-lithography and in Topas by Daniel Nilsson using Nanoimprint lithography. The imprinted laser has been characterized in [76]. Fig. 6.4 shows a design image of the microfluidic dye laser. The in- and outlet are 5000 μm long, and the diameter of the half circles at the end of the in- and outlet is 2500 μm. The laser cavity is 1000 μm × 1000 μm. The cavity is made up of an array of parallel microfluidic channels, thus forming a Bragg diffractive mirror. The channels are 22.4 μm wide and separated by 21.5 μm wide walls. The array can be divided into three areas. The first and third area are two arrays of 11 microfluidic channels and walls each 22.4 and 21.5 μm wide respectively. They are separated by the second area, which is a single phaseshift channel, e.i. the cavity is made up of 23 channels in total. The phaseshift channel is introduced, to remove the degeneracy of the resonance in the laser
cavity, thus only the Bragg resonance frequency is amplified. The phasishift channel is \( \frac{1}{4} \)

wider than the other channels, i.e. 21.61 \( \mu m \), as the laser cavity was designed for Ethanol to

be used as laser medium. In Fig. 6.4 the laser cavity is shown together with the in and outlet.

In order to avoid stray light or fluorescence from the inlets, fluorescence blockers were placed

on each side of the inlets. The fluorescence blockers are placed 200 \( \mu m \) from the inlet and

are 200 \( \mu m \) wide. Their length are equivalent to the length of the inlets. The fluorescence

blockers are inspired by a similar design from the so called "ultimate chip" project [19]. The

fluorescence blockers can be seen in the final chip layout in Fig. 6.9.

6.1.4 Lenses

To fulfill the requirements listed in Sec. 6.1, a sort of focusing system is needed, as laser light

is emitted along the 1000 \( \mu m \) cavity of the microfluidic dye laser. Different solutions were

considered and three are shown in Fig. 6.5. In Fig. 6.5 A), the light is collected by many

waveguides at the edge of the laser cavity, most of these waveguides are guiding the light away,

and a single one is guiding the light to the absorbance cell. The obvious drawback is,

that most of the light is guided away and not used for measurements, thus the intensity of

the light at the detection area is small. Fig. 6.5 B) shows a system with two lenses. The first

lens focusses the light onto the second lens, which focusses the light into the waveguide. By

using two lenses the light in the waveguide should be somewhat collimated. The drawback of

this system is that two lenses are needed, thus increasing the number of polymer/air interfaces

the light has to pass through the device. Fig. 6.5 C) shows a system with a single lens, that

focusses the light directly into a waveguide, where the light is guided by internal reflection.

The major concern in this design, is that the light that is focussed into the waveguide, must

remain inside the waveguide, to do so the incidence angle must be smaller than the critical

angle for internal reflection. As the lenses will be made up of air cavities on the chip, some

anti-guiding of the light will occur, as the cavity will be sealed between two substrates with

a higher refractive index than air. Therefore it is desirable to fabricate the lenses as narrow

as possible, thus minimizing this effect. An interesting approach is the use of Fresnel lenses,
as they are very slim compared to conventional lenses. In Fig. 6.7 a conventional lens is

compared to a Fresnel lens, where both lenses have the same height and focal length, so the

main difference is the width and volume of the lenses. Both lenses are narrow at the center

and very little anti-guiding takes place, i.e. situation b) and d) in Fig. 6.7. The conventional
CHAPTER 6. DESIGN AND FABRICATION

Figure 6.5: Three different solutions for focusing the light from the micro cavity fluidic dye laser. The light paths are indicated by green arrows. A) The light collected by different waveguides, one leads the light towards the absorption cell, and the rest of the light is guided away. B) The light is focussed through two lenses, the first focuses the light to the small lens, and the small lens focuses the light into the waveguide. C) A single lens focuses the light directly into a waveguide.

The side of the Fresnel lens, that is facing away from the laser cavity, the saw teeth are sloped, such that they do not block the light that is focussed by the lens. The angle of the slope is adjusted such that it fits the angle the light is deflected by the lens. The is seen in Fig. 6.6, where the light path is illustrated by green arrows. A sketch of the entire Fresnel lens is shown in Appendix E, where the dimensions of the Fresnel lens is listed.

A SEM image of the imprinted Fresnel lens and laser cavity is seen in Fig. 6.12(a), where the focusing of the emitted laser light is illustrated.

6.1.5 Waveguides

The waveguides used in this project are 20 μm wide and 10 μm high. This makes the waveguide multimode, but as the height of the imprinted structures determines the height of the waveguide, one may need to fabricate a wide waveguide in order to have an appropriate aspect ratio. The waveguide is embedded between a Pyrex glass lid and a SiO₂ substrate in the vertical direction, and surrounded by air in the horizontal direction. The air filled groove on each side of the waveguide is 50 μm wide. The curved sections of the waveguides have a radii of curvature of 5500 μm.
Figure 6.6: Sloped saw tooth of the Fresnel lens. The angle of the cut matches the angle that the emitted light is deflected by the lens, such that the lens does not shade the emitted light.

Figure 6.7: Comparison of a conventional lens with a Fresnel lens. At the center of both lenses, the anti-guiding effect is the same, situation b) and d). At the end of the lenses the situation is different. The conventional lens, situation a) will have a much higher loss, due to anti-guiding, as the lens is wider at the end, than the fresnel lens, situation c).
6.2 Chip layout: Lab-on-a-chip for absorbance measurements

In Fig. 6.8 several design considerations are shown, and stray light is illustrated with red arrows and focussed laser light is illustrated with green arrows. In situation A the absorbance cell is placed right in front of the laser, and the focussed laser light is guided by a strait waveguide. The drawback is that stray light is also guided to the absorbance detection cell and may interfere with the measurements. In situation B the absorbance cell is placed away from the microfluidic dye laser, and a curved waveguide, guides the light to the absorbance cell. The stray light will (ideally) continue away from the laser and not interfere with the measurement. When operating curved waveguide one must remember to have a high radius of curvature, in order not to lose too much light through radiation loss, see Sec. 4.3.4. As the position between the laser and the absorbance cell had been determined the focus was moved to the design of the entire chip. Some requirements was set up for the design: The distribution of protrusions on the stamp should be as homogenous as possible, in order to avoid to much bending of the stamp, and thereby achieve a more homogenous thickness of the residual layer. Given the size of some of the structures, i.e. the laser inlets, it would be very difficult to get exactly the same protrusion coverage across the stamp, but the structures on the device must be distributed such that the protrusion coverage is as homogenous as possible. Another requirement is that the laser cavity must be somewhat easily accessible, as the pump laser beam will have a sloped trajectory towards the device, so a small vertical hole in the device holder for the pump laser beam is not desirable. Furthermore the inlets of the device must be placed in such a way that they do not interfere with the optical measurements, e.g. there should not be an inlet on the side of the chip holder, where the optical measurement is made, as it would limit the number of possible positions where an optical fibre could be placed. Finally it would be desirable to have a high number of devices per wafer, in order to exploit the fact that we can make wafer scale NIL. In Fig. 6.8 C and D two different schematic illustrations of chip designs are shown. The green arrows show the light path of the chip. The main difference between the chip design shown in C and D, is that the design in D, is more homogenous than the one shown in C, with regards to distribution of structures. Furthermore the design shown in C has two inlets placed between the optical outputs of the chip, whereas the design shown in D only has one. The design in C is also considerably larger than the one shown in D, this is not very well shown in the illustrations but calculation showed that the chip would be bigger and it would be difficult to have more than two chip per wafer. The design shown in D is smaller than the one shown in C, as the microfluidic dye laser is tilted 45° and the waveguides therefore take up less space. Furthermore the protrusions could be distributed (almost) evenly across the device, and as the microfluidic dye laser was placed near the edge, easy access to the laser cavity for the pump laser beam would be possible. The final layout of the chip is shown in Fig. 6.9 and the layout for the entire stamp can be seen in Appendix D.

6.3 Chip layout: Lasers for lens investigations

This device is fabricated with the purpose of investigating the functionality of a conventional lens and a Fresnel lens. The need for such a device came after the observations described in Sec. 7.2.3. The laser cavity and Fresnel lens used in this device is exactly similar to the
Figure 6.8: A and B shows the difference in using strait or curved waveguides to guide the light to the absorbance cell, e.i. the small black square. Stray light is illustrated by red arrows and the emitted light by green arrows. When using a strait waveguide the stray light from the laser cavity will also reach the absorbance cell, whereas as curved waveguide will (ideally) make sure only the laser light (green arrow) is guided to the absorbance cell. C and D shows two different suggestions for the design of the entire chip. The green arrows shows the light path. The device fabricated in this project was made using the design sketched in D.

Figure 6.9: The final layout for the LOC device for absorbance measurements. The layout of the entire stamp can be seen in Appendix D. Note the fluorescence blockers on each side of the inlets for the microfluidic dye laser.
one used for the LOC for absorbance measurements. The conventional lens has the same length as the Fresnel lens, the same width at the center and the same focal length, such that a comparison of the functionality between the two types of lenses is possible. In Fig. 6.10 the layout of the device is shown. The device has two methods for monitoring the functionality of the lenses. The first involves dicing the devices at designated distances from the lens, and then measure the intensity of the focussed laser light along the side of the chip using an optical fibre. For this dicing marks have been made and the inlet has been made parallel to the dicing marks at this side. The fluorescence blockers have been maintained unaltered. The second method is by fluorescence in a fluorescent liquid. A large reservoir is made to the other side of the laser cavity and when filled with a fluorescent liquid, the light path of the laser light should be visible. The laser cavity is placed in the horizontal direction, such that completely smooth sidewalls and single mode lasing may be achieved. A SEM image of the laser cavity is seen in Fig. 6.12(d) and the completely smooth sidewalls may be observed. The layout for the entire stamp is shown in Appendix D.

6.4 Fabrication

In this section the fabrication scheme for the devices fabricated in this project is presented. The fabrication scheme is similar for all devices fabricated in the project.

6.4.1 Stamp fabrication

The first step in the fabrication of a NIL stamp is a 30 s. HF-etch, afterwards a 1.5 μm thick layer of AZ5214E photoresist is spun onto the wafer. Prior to UV-exposure the mask is treated with Hexamethyldisilazane (HMDS) in order to avoid adhesion between the quartz mask and the photoresist. The photoresist is patterned by conventional UV-lithography, using Hard Contact mode. The photoresist is developed in AZ351B developer for 1 min, followed by a rinse in DI-water for 4 min. The pattern is now defined in photoresist and needs to be transferred to the silicon. Immediately before the Silicone etch, the wafer is exposed to a HF-etch for 30 s, followed by a rinse in DI-water for 4 min. The pattern is transferred to the silicon
Figure 6.11: Process sequence for the fabrication of stamps and subsequent imprint and bonding. 1-3 The pattern is defined by standard photolithography in AZ5214E photoresist. 4-5 The pattern is transferred to silicon by an advanced silicon etch, using an optimized BOSCH process. 6-7 A thin oxide layer is grown on the stamp and subsequent removed by a selective wet etch. 8 An anti-sticking layer is deposited on the stamp. 9 The substrate, a Silicon wafer with a 3 μm thick SiO$_2$ layer, is coated with a 10 μm thick Topas film. 10-12 The stamp is imprinted into the substrate and the pattern is transferred. 13 The residual layer is removed by an oxygen plasma in a Reactive Ion Etching tool 14-15 A Pyrex glass lid is cleaned and coated with a thin topas layer and a thick protective layer of photoresist. 16-18 The inlet holes are fabricated by sandblasting through patterned adhesive tape. 19 The imprinted pattern is thermally bonded to the glass lid.
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wafer using a Deep Reactive Ion Etching (DRIE) tool, and the optimized BOSCH process [77], which has a cyclic nature. Each cycle consist of an etch and a passivation step. The optimized etch process, produces steep sidewalls with a roughness below 50 nm. A standard process normally produces a roughness around 300 nm. Following the silicon etch, the photoresist is removed in an acetone bath. The stamp is cleaned following a RCA cleaning procedure, ensuring the surface of the stamp is completely clean [78]. Immediately after the RCA clean, the stamp is placed in a furnace, where a 450 nm thick oxide layer is grown, using a wet thermal oxidation process. The oxide layer is removed in a HF-etch and the stamp is cleaned in DI-water for 4 min. The growth and subsequent stripping of oxide will smoothed out the scallops from the cyclic silicon etch, thus ensuring a smooth vertical sidewall of the stamp. Smooth sidewall is a requirement if one wants to achieve easy separation of the stamp after the NIL process. Furthermore optical applications require smooth sidewalls in order to reduce scattering. Prior to imprint the stamp is coated with an anti-sticking coating, using one of the recipes described in Chap. 3.

6.4.2 Substrate

The substrate, in our case a silicon wafer with a 3 μm thick thermally grown oxide layer, is coated with a 10 μm thick Topas film. Topas is supplied in a solid pellet form, and has to be dissolved in a nonpolar solvent prior to spin coating. We use Toluene, and a 23 wt % solution of Topas grade 8007 is prepared. The dissolution of the Topas pellets are aided by placing the closed container under Ultra Sonic (US) agglomeration for 24 hours. Prior to coating the substrate is baked at 150 °C for 10 min. Approximately 5 ml of the Topas solution is applied at the center of the wafer, and the wafer is spun at 2000 rpm for 60 s. The spin process is followed by a bake at 150 °C for 10 min, thus removing the toluene completely.

6.4.3 Imprint

Imprints made in Thrya

The stamp and Topas coated substrate are placed face to face, in the imprint machine. In order to ensure a homogeneous distribution of pressure, a PDMS mattress is placed on top of the stamp. A dummy wafer is placed on top of the PDMS mattress, thus it does not adhere to the chuck of the imprint machine, see Fig. 3.9 A. The chamber of the imprint machine is pumped down, and the chuck is heated to 200 °C, when the designated temperature is reached the stamp and substrate are pressed together using an imprint force of 2000 N on a 4 inch wafer. The imprint time is 5 min. The stamp and substrate are cooled, and when the temperature is below $T_g$ of the Topas, they are removed from the imprint machine and placed on a table, where they quickly cool to room temperature. The stamp is gently separated from the substrate using a scalpel.

Imprints made in EVG 520EH

The stamp and Topas coated substrate are placed face to face, in the imprint machine. In order to ensure a homogeneous distribution of pressure, two flexible graphite sheets are inserted
between the stamp/substrate and the chucks of the imprint machine. See Fig. 3.9 B, where the setup inside the imprint machine is illustrated. The chamber of the imprint machine is replaced with a dry Nitrogen atmosphere, and the chucks are heated to 200 °C, when the designated temperature is reached the chamber is evacuated, and the stamp and substrate are pressed together using an imprint force of 15000 N on a 4 inch wafer. The imprint time is 5 min. The stamp and substrate are cooled, and when the temperature is below $T_g$ of the Topas, they are removed from the imprint machine and placed on a table, where they quickly cool to room temperature. The stamp is gently separated from the substrate using a scalpel.

6.4.4 Removal of residual layer

Prior to bonding the residual layer of the imprinted structure is removed by an oxygen plasma in a Reactive Ion Etching (RIE) tool. The recipe for removal of the residual layer is adapted from [7]. Due to the spin process the residual layer of the imprinted structures is relatively high, e.g. 0-3 μm and therefore a long etch time is necessary. The temperature in the RIE tool during the etch can exceed $T_g$ of the Topas, therefore the oxygen plasma is applied for a limited period, hence 30 s, and then the substrate is allowed to cool before the process is repeated. During the cooling process the substrate is transferred from the RIE chamber to the load lock of the RIE tool, thus allowing a visual inspection of the substrate. If the residual layer has been removed, it is possible to see the SiO$_2$ and the process may be stopped.

6.4.5 Preparation of lids for bonding

Bonding using a homemade solution of Topas grade 9506

A pyrex glass wafer is cleaned in X100 detergent and DI-water under US aggregation for 10 min, followed by a 7-UP etch (sulphuric acid and ammoniumperdisulfate at 80 °C). Prior to spin coating the Pyrex glass wafer is baked at 150 °C for 10 min, thus dehydrating the surface. Approximately 3 ml of the homemade Topas solution, here a 5.5wt % of Topas grade 9506 in Toluene is applied to the wafer. The wafer is spun at 6000 rpm at 60 sec. The coated wafer is baked at 150 °C for 10 min. The Pyrex wafer is imprinted with a flat stamp at 120 °C using normal imprint parameters, thus levelling the spin coated surface, see Sec. 6.5.4.

Bonding using a commercial solution of Topas grade 9506

A pyrex glass wafer is cleaned in X100 detergent and DI-water under US aggregation for 10 min, followed by a 7-UP etch (sulphuric acid and ammoniumperdisulfate at 80 °C). Prior to spin coating the Pyrex glass wafer is baked at 150 °C for 10 min, thus dehydrating the surface. Approximately 2 ml of the Topas, here a 6.5 wt % Topas grade 9506 in SecButylBenzene, which is supplied by Microresist [79] is applied to the Pyrex wafer. The wafer is spun at 6000 rpm at 60 s, thus forming a 200 nm thick Topas layer.
6.4.6 Fabrication of inlet holes

Drilling inlet holes

This fabrication step usually took place after the imprinted structures had been bonded and diced out, but nevertheless it is presented here, as this is the place in the process sequence for the new method for fabrication of inlet holes, see the next paragraph. The diced out chip is placed in a small petri disc, and covered with DI-water. A diamond drill, 800 μm in diameter, is used to drill through the Pyrex lid. The water acts as cooling for the drill and also removes some of the material that has been drilled out. A major drawback of this method is the low yield of the process, as many inlet holes are either unusable or very difficult to get any liquid through the inlets due to clogging. The diamond drill needs to be replaced after having drilled about 30 holes, as it is worn out.

Sandblasting inlet holes

The side of the lid, that is coated with a thin Topas film, is covered with a 10 μm thick layer of AZ4562 photoresist. The photoresist is softbaked at 60 °C for 20 min. The front and backside of the lid is covered with an adhesive film and the adhesive film is patterned with a CO2 laser. The openings in the adhesive film is used as masking for a sandblasting process. The sandblasting is made with 90 μm large alumiumoxide particles, and cone shaped inlet holes with a diameter of approximately 400 nm are created. Each holes takes about 10-15 s to sandblast. The lids are cleaned using DI-water and the adhesive film is removed. Before the protective layer of photoresist is removed in acetone, the lids are rinsed in DI-water for 5 min.

6.4.7 Bonding

The bonding process is similar to the imprint process and only the temperature and the force is changed. The imprinted structure and the lid is placed face to face inside the machine using the same setup as for imprints, see Fig. 3.9 for details.

Bonding using Thyra

The bonding temperature is 65 °C using a bonding force of 2000 N on a 4 inch wafer. The bonding time is 5 min and the force is released when the temperature is lower than 45 °C. It is observed that the temperature controllers on Thyra have a slight overshoot at this temperature range, thus damaging the imprinted structure if the bonding is not made very carefully.

Bonding using the EVG 520EH

The bonding temperature is 70 °C using a bonding force of 5000 N on a 4 inch wafer. The bonding time is 5 min and the force is released when the temperature is lower than 45 °C.

6.4.8 Imprint results

Part of the objective for this thesis was to develop a process recipe for fabrication of imprint in Topas grade 5013. When a proper anti-sticking layer is applied to the stamp, it is possible to
fabricate imprints in Topas grade 5013, by using the same imprint conditions as for Topas grade 8007. However, the imprint time needs to be increased to 10 min, but all other parameters are unchanged. As Topas grade 5013 was susceptible to ESC, see Sec. 6.5.2, the work in this thesis was done in Topas grade 8007, and the imprint time is therefore set to 5 min in this thesis. If devices are to be imprinted in Topas grade 5013, the imprint time must be set to 10 min if good results are to be obtained. Scanning Electron Microscope (SEM) images of the imprinted devices are shown in Fig. 6.12. The imprinted LOC device is shown in Fig. 6.12(a) where the laser cavity, Fresnel lenses and waveguide are shown. As the laser cavity is turned 45° with respect to the horizontal direction the mask may have small scallops along the side of the sloped structures, and these scallops are transferred to the imprinted structures, as shown in Fig. 6.12(b). An example of the imprinted laser devices for lens investigations is shown in Fig. 6.12(c) where a conventional lens is seen next to a laser cavity. As the laser cavity in this design is placed in the horizontal direction completely smooth sidewalls may be fabricated as seen in Fig. 6.12(d).

6.5 Discussion of fabrication issues

In this section the different issues regarding the fabrication will be discussed.

6.5.1 Homogeneity of spin coated polymer films

When this project took off, no commercially solutions of Topas was available, and therefore the Topas solutions used are homemade. A parallel project by Theodor Nielsen et al. in cooperation with Microresist [79], investigates which solvents that are optimal for spin coating of Topas [80]. When spin coating, using the homemade Topas solutions, the surface roughness of the spin coated surface is quite high and the thickness of the Topas film is very uneven. The thickness of a Topas film, spin coated from a 23 wt\% solution of Topas grade 8007 dissolved in toluene, has been observed to vary from 6.7 μm up to 13.4 μm on the same wafer, but usually the variation is between ± 1.5 μm. During the fabrication it was observed, that when the average height of the Topas layer is the same as the height of the protrusions on the stamp, holes appeared in the imprinted structures.

In order to avoid such holes in the imprinted structure, the Topas layer has, on average, to be a bit higher than than the stamp protrusions. This will eventually lead to a higher residual layer, but it is a consequence of using the home made Topas solutions. It is clear that the holes originate from the polymer flow during the imprint process and a SEM image of such holes can be seen in Fig. 6.13. The holes are always observed near imprinted structures, as the polymer flow is mainly taking place near the protrusions. A result of the uneven Topas layers is that the residual layer of the imprinted devices is high. The first investigations of the thickness of the residual layer indicated a thickness around the the cutoff thickness for the zeroth order optical mode. However later and more thoroughly investigations showed another picture, as the residual may change from around 450 nm up to 4.4 μm within the same device. An example of such an investigation is shown in Fig. 6.14, where the measuring points are indicated by black arrows. The thickness of the residual layer vary from 450 nm up to 4.4 μm
(a) The imprinted LOC structure, the functionality of the fresnel lens is shown by the light path.

(b) Grooved surface due to the mask production.

(c) Laser cavity with conventional lens.

(d) Laser cavity with perfectly smooth sidewalls when placed in the horizontal or vertical direction.

Figure 6.12: SEM images of different imprints.
Figure 6.13: SEM image of holes in imprinted structures. The holes originate from lack of polymer and are always observed near imprinted structures, as the polymer flow mainly takes place here.

within the area of a single device. The thickness of the residual layer at the measuring points are listed in the caption of the illustration.

It goes without saying that residual layers of thickness's comparable to the cutoff conditions for waveguiding was observed, however it is considered a lucky punch to fabricate a device where the overall thickness of the residual layer does not limiting the operation of the device.

It goes without saying that not all devices have so thick residual layers, e.g. one of the other devices on the same wafer, the residual layer was much thinner than on this device, and many of the measured thicknesses were below the cutoff thickness for the zeroth order mode, thus it is possible to fabricate devices, where the thickness of the residual layer is not limiting the operation of the device.

6.5.2 Environmental Stress Cracking

While processing wafers with Topas grade 5013 it was observed that cracks are induced in this Topas grade, when exposed to acetone, iso-propanol or photoresist. These cracks are interpreted as an indication of Environmental Stress Cracking (ESC), which is a physical process and does not involve any chemical degradation of the polymer. ESC was not observed for Topas grade 8007 and 9506 when exposed to acetone, iso-propanol or photoresist. As ESC is a physical process, data on chemical compatibilities does not give any information on ESC behavior. In order for ESC to take place two requirements are needed. 1) Stress must be induced in the polymer, and the stress levels in the polymer must be above a certain minimum, or critical stress level. 2) The polymer must be exposed to a liquid environment. When these requirements are fulfilled ESC may take place. The process that is suspected to lead to ESC, is the formation of very small voids on the polymer surface, < 30 nm. When
the polymer is exposed to a liquid environment, the molecules in the liquid diffuse into the void and locally plasticizes the polymer, thus reducing the strength of the material at that point. This leads to a larger and deeper crack and more molecules are able to diffuse into the crack and the new volume in front of crack, which is exposed to the liquid, experience plasticization and the process is repeated. For a review of ESC and deeper explanation of the process [81] and [82] are recommendable. Several attempts to predict ESC by different solubility parameters have been published [83, 84]. Some correlation between the so called RED value\(^1\) and the molecular volume has been observed, but a reliable prediction is not yet available [84]. For COCs a crude rule of thumb may be extracted from the studies. It appears that large and bulky, or ring shaped molecules does not cause ESC, while smaller and linear molecules may cause ESC, when sufficient stress is induced. In our case the stress is induced by the temperature cycle of the imprint process due to thermal mismatch between the silicon substrate (\(\alpha_{\text{Si}} = 2.6 \times 10^{-6} \text{ K}^{-1}\)) and the Topas film (\(\alpha_{\text{Topas}} = 0.6 \times 10^{-4} \text{ K}^{-1}\)). Several attempts were tried in order reduce the level of induced stress in the polymer film, such as slow cooling of the imprinted structures, and crack healing of cracked polymer films by heating them to above \(T_g\). One of these investigations is shown in Fig. 6.15. Here Topas grade 5013 dissolved in toluene is spin coated onto a silicon wafer. The surface after spin coating is shown in Fig. 6.15 A). The images are taken at the edge of the wafer, so it is possible to find the same location again. Fig. 6.15 B) shows the cracks after a 2 min exposure to Iso-Propanol (IPA). The cracks are healed by placing the wafer on a 150 °C hotplate for 2 min. As seen in Fig. 6.15 C) this procedure removes the cracks, and in order to reduce the stress levels the wafer is slowly cooled to room temperature. A subsequent exposure to IPA induces new cracks

\(^1\)Relative energy difference, see [83].
in the Topas as seen in Fig. 6.15 D). This investigation is also interesting, as it shows how one is able to remove the thermal history of a polymer by heating it to above $T_g$. This is seen in Fig. 6.15 D) where the cracks appear at new locations after the second exposure to IPA. None one of attempts to reduce the stress levels in the Topas film were successful, and the main conclusion is: when processing structures in Topas films on silicon substrates, one should use Topas grade 8007, as the induced stress levels are smaller due to the low $T_g$ of Topas grade 8007. Due to ESC in Topas grade 5013 it was decided to fabricate the LOC device in Topas grade 8007 and seal it with an intermediate layer of Topas grade 9506.

During operation of the finished devices, ESC was observed in Topas grade 8007, when exposed to Ethanol for long periods (+6 hours). The cracks allowed the laser medium access to the to the Fresnel lenses, thus making the device useless, as the functionality of the lenses had been destroyed, see Fig. 6.16. The solution was to change the laser medium to Ethylene Glycol, as no ESC was observed in Topas grade 8007, when exposed to Ethylene Glycol. This
fits well with the crude rule of thumb for ESC in COCs, as the Ethylene Glycol molecule is bigger than the Ethanol molecule.

6.5.3 Removal of the residual layer

The thickness of the residual layer is to thick to fulfill the cutoff condition listed in Sec. 4.3.3 and therefore it is necessary to remove the residual layer. The Reactive Ion Etch used for the removal of the residual layer, is directly adapted from [7], where the etch rate in Topas grade 8007 has been measured to 12 nm/s. As the residual layer is quite thick for the fabricated devices, a long etch time is required. The first etches had an etch time of 4 min, corresponding to a removal of approximately 3 μm of Topas. Unfortunately the processing temperature of the RIE chamber exceeded $T_g$ of the Topas and reflow of the imprinted polymer structures took place, see Fig. 6.17(a). In order to reduce reflow the process was changed to a cyclic process, that changed between an etch step and a cooling step. During the cooling step, it is possible to inspect the imprinted structures and if the substrate material is visible, the process may be stopped. The etch time of the etch step is 30 s. During the oxygen plasma a surface modulation takes place, see Fig. 6.17(b) and small polymer particles may be found on the surface. It has not been possible to make SEM images of imprinted structures where no reflow has taken place during the cyclic RIE process, as there were not enough time to fabricate extra wafers for SEM investigations.

6.5.4 Bonding issues

The Topas layers that are spin coated from the homemade solutions has a high surface roughness and therefore such layers can not be used directly for bonding. The reason is that the bonding process is not able to adapt for the short range surface roughness, and the imprinted structures will only bond to the thickest areas on the lid, thus creating nano-sized channels between the imprinted structures and the intermediate bonding layer. Such channels will allow
access for the laser medium to the Fresnel lenses making the device useless. By imprinting the spin coated Topas film with a flat stamp, it is possible to reduce the surface roughness by up to two orders of magnitude. For Topas grade 8007 dissolved in a 23wt % solution in toluene, the surface roughness was reduced from 400-600 nm down to 4-6 nm. For Topas grade 9506 dissolved in a 5.5wt % solution in toluene the surface roughness was reduced from 40-50 nm down to 5-7 nm. The surface roughness have two components, a short range component and a long range component. During levelling, the short range component is smoothed out, due to polymer flow, but the long range component is almost unaffected by the levelling, as the polymer transport over long distances are not likely to take place during the relative short time of the levelling process. During the levelling process the flexibility of the silicon stamp adapts for the long range surface roughness, and smooths out the short range surface roughness, thus fabricating a surface that is completely levelled on the short range. In a subsequent bonding process the flexibility of the silicon substrate and the Pyrex lid, will adapt for the long range surface roughness, thus insuring a good bonding.

Another bonding issue is temperature control. During the initial bondings in Thyras the temperature controller was not connected correctly, thus the temperature controllers showed a temperature approximately 10 °C lower than the actual temperature on the ducks. This gave rise to some problems during the bonding process, as the imprinted structures were damaged and the devices made useless. When the error was detected and the temperature controller was connected correctly, the PID values of the imprinter was not optimized, thus a very large overshoot was observed for temperatures below 100 °C. It has been observed that the Fresnel lenses are most sensitive to reflow during the bonding process, this is reasonable as the Fresnel lenses are the narrowest structures on the devices. In Fig. 6.18 examples of a successful and an unsuccessful bonding are showed. In general the bonding yield was acceptable, but the introduction of an oxygen plasma to remove the residual layer, seemed to lower the yield, but not enough data is available to make a clear assessment.
6.5.5 Clogging of inlet channels

A major problem has been clogging of the inlets after holes have been drilled through the lid of the device. The clogging may be due to small Pyrex or Silicon particle that have been drilled out, or the small gap between the Topas layers may simply have been blocked by a piece of Topas, that had gone loose during the drilling. In order to investigate how the drilling procedure affects the Topas layer, a device was diced through and the cut was investigated using a Scanning Electron Microscope. In Fig. 6.19 C) the SEM image is shown. One is able to see how the glass fractures at the bottom of the Pyrex glass wafer, which is seen as sloped cracks at each side of the hole. One may compare with the optical image of a drilled inlet hole, which is shown in Fig. 6.19 B. Furthermore it is seen how the Topas layers are torn up from the substrate, and they may clash together, thus blocking the inlet. When the inlets are drilled there are usually problems with two to four of the six inlets on the device, usually one or two are blocked and the remaining is very hard to get liquid through. If the yield of the drilling process is set to around 70% for a single hole, there is a 10% chance for fabricating a device with six inlet, where no inlets are blocked. When fabricating device with two to three inlets, a yield of 70% per drilled hole is acceptable, but for devices with more inlets the yield needs to be higher. A solution was to sandblast the inlet holes prior to bonding. In Fig. 6.19 A an optical image of a sandblasted hole is seen, and there is no particles left from the sandblasting process. The particles at the bottom of the hole originate from the dirty environment in the optical laboratory. The sandblasting process has several advantages over the drilling process, first the microfluidic channels are not clogged due to dust particle as the inlet holes are made in the lid prior to bonding. Secondly the Topas layers are not twisted or torn apart and therefore a very clean and smooth inlet may be fabricated, furthermore it is very easy to get liquid through the holes. The yield for sandblasted holes is 100%, and literally every inlet hole that has been sandblasted and tested has worked flawlessly. The change in fabrication method for the inlet holes also reduced the problem with bubbles in the microfluidic channels significantly.

A chip where the inlets have been sandblasted has also been sent for dicing in order to
Figure 6.19: Optical and SEM images of inlet holes.  

A Optical image of a sandblasted inlet holes.  

B Optical image of a drilled inlet hole, note the fracturing of the glass lid.  

C SEM image of a cross section of a drilled inlet hole. The device has been diced through the drilled inlet hole. Note the piece of polymer that sticks out, where the liquid is supposed to pass through, when the hole is being filled.
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Figure 6.20: Poor adhesion between imprinted structures in Topas grade 8007 and a Quartz wafer. The images is taken after removal of the residual layer and sandblasting of inlets. The release took place during removal of the protective layer of photoresist, that was applied before the sandblasting. The remaining channels in the laser cavity are held in place by the residual layer, which, in this case, was not completely removed. The black arrow shows the edge of the remaining residual layer.

make a SEM investigation, but unfortunately it has not been diced at the deadline for this report.

6.5.6 Adhesion problems to Pyrex and Quartz

During the project it was observed that Topas had poor adhesion to Pyrex wafers, which are used as lids. It was observed to take place during dicing of the wafers, where the glass lid simply came off during the dicing process. It was clear that the release took place between the intermediate bonding layer and the pyres glass lid, as the intermediate bonding layer was still covering the device, and the inlet holes that was sandblasted through the intermediate layer was clearly visible. It seems that Topas adheres better to SiO₂ than to pyrex, even though the Pyrex wafer has been given the same surface treatment prior to spin coating, i.e. a 10 min 7-UP etch and a bake at 150 °C for 10 min. Therefore it was decided to use a SiO₂ wafer coated with a thin layer of Topas grad 9506 as a lid, and imprint the structures on a transparent wafer. As the residual layer had to be removed in the RIE-tool at MIC, it was necessary to use a Quartz wafer instead, so the RIE-chamber was not polluted by the additives in the Pyrex wafer. The Quartz wafer was given the same surface treatment as the lid, i.e. a 10 min 7-UP etch and a bake at 150 °C for 10 min prior to spin coating. There was no sign of any adhesion problems during the imprint, removal of residual layer and sandblasting of inlet holes. However, when the protective layer of photoresist had to be removed after the sandblasting, release of the imprinted structures was observed. This is shown in Fig. 6.20. From visual inspection through a microscope it is clear that all the narrow structures, such as microfluidic channels in the laser cavity and waveguides have released. In one of the laser
cavities the residual layer has not been completely removed and some of the channels was still attached to the residual layer. In Fig. 6.20 it is seen how the edge of the residual layer holds the channels in place. Similar effects are observed for the waveguides which are held in place at each end, where they have contact to the "bulk" of the polymer film. Poor adhesion was primarily observed for lids which had been coated with the Topas solution from Microresist, but the data are not sufficient to make a clear assessment. Poor adhesion was only observed for Pyrex or Quartz surfaces, and one may look into adhesion promoters, such as HMDS, which are usually applied to Pyrex or SiO$_2$ wafers before any photoresist is spun on.

A different surface treatment was also tried in order to increase the adhesion between Pyrex and Topas. Following the 7-UP etch the Pyrex wafer was exposed to a 6 min HF etch, however no change was observed.

### 6.6 Summary

An integrated LOC for absorbance measurements have been designed and fabricated by NIL. Devices have been fabricated in both Topas grade 8007 and 5013, and it has been shown that in order to fabricate good imprints in Topas grade 5013, the imprint time needs to be increased from 5, to 10 min., thus there is no need for further changes in the imprint process. Due to ESC in Topas grade 5013, the work was mainly made using Topas grade 8007.

The first many batches of the LOC had fabrication problems such as poor yield of the inlets holes, and a new method for fabrication of inlet holes were introduced. The devices that were fabricated in the first many batches in this project was destroyed due to ESC, as the laser medium had not yet been changed to Ethylene Glycol. The change from Ethanol to Ethylene Glycol increased the survival time of the devices considerably. As the optical measurements progressed it became clear that the residual layer had a considerable impact on the results and therefore had to be removed. The introduction of the process step, where the residual layer is removed by an oxygen plasma in a RIE-tool did also take some time, as as the process had to be tuned for the rather thick residual layers, which were experienced in the project. Furthermore the bonding yield seemed to go down when the imprinted structures had been RIE-etched prior to bonding.

Two serious problems have slowed down the project. The first is an adhesion problem, as the lid seemed to release from the intermediate layer during the dicing of the wafers. The only known working cure against this problem is to try again, but improvements have to be made, for the technology to be fully matured. The second problem was the lack of dicing facilities at Danchip. From mid December to late July, it was not possible to dice Pyrex wafers at Danchip and all dicing took place at Birkkerød, where laboratory technicians were allowed to use the dicing facilities. The dicing was not very regular and for every batch of wafers, one to two weeks of waiting time was expected. This was a serious problem and much more work could have been done if proper dicing facilities had been present at Danchip. The lasers for lens investigations were designed late in the project, and unfortunately the bonding of the fabricated devices was not good enough, and it was not possible to make any measurements.
CHAPTER 6. DESIGN AND FABRICATION
Chapter 7

Optical measurements

This chapter presents the optical measurements made on the fabricated LOC devices. The first section describes the measurement setup and the equipment used to make the measurements. Thereafter follows the optical characterization of the microfluidic dye laser, and some preliminary absorption measurements, which demonstrates the functionality of the LOC. Finally the importance of removing the residual layer and light control is demonstrated.

7.1 Experimental setups

In order to ensure tight fluidic connections a device holder is fabricated in poly-carbonate, which is sold under the commercial name Lexan. The device holder is seen in Fig. 7.2(a) and consist of two plates, that are pressed together by screws at each corner. The top plate contains the in- and outlet connections which are made of 1 mm thick syringe needles, the connections between the device and the device holder is fitted with O-rings that prevents any leaks. An access hole for the pump laser beam is made in the top plate. When the device is mounted in the device holder, it is placed in the setup which is outlined in Fig. 7.1. A pulsed frequency double Nd:YAG laser (Surelite continuum I-10) with a primary wavelength of 1064 nm and a secondary wavelength of 532 nm is used as pump laser. The pulse length is 5 ns and the frequency is 10 Hz. The laser light is split by a frequency splitter and the second harmonic is damped by an attenuator whereafter it is guided to the opening in the device holder by the use of mirrors. The beam passes a 1.5 mm split on its way round the optical table, in order to decrease the spot size, so it fits the size needed on the device, e.i. the area of the laser cavity, which is 1 by 1 mm. The surface of the device and the device holder is colored black in order to prevent any stray light to interfere with the measurements, i.e. stray light that reaches the inlets for the microfluidic dye laser may create fluorescence. The pump laser beam is scattered due to the fact that the mirrors are not 100 % perfect. Such a situation is seen in Fig. 7.2(b), where a device is placed on a white piece of paper, and the laser beam is focused on the laser cavity. The surface of the device has been colored black, and only the circumference of the scattered light is visible. During operation the laser medium is pumped through the microfluidic dye laser by an external syringe pump (Harvard 11Plus), the used laser medium is collected in a waste tank. The buffer solutions are manually pumped through
CHAPTER 7. OPTICAL MEASUREMENTS

Figure 7.1: Schematic illustration of the optical setup at the optical table in the basement. Inside the dotted box the view changes from top view to sideview.

the absorbance cell using syringes. The syringes and the syringe pump are connected to the device holder by flexible rubber tubes. Two different measuring setups where used during the project and they are each described in the following sections.

7.1.1 Setup A

The device is placed in the device holder, which is placed on an adjustable table. The mirrors are adjusted, so the light beam is focussed onto the laser cavity on the device. With another adjustable table the optical fibre is moved into position directly in front the waveguide exiting the laser, see Fig. 7.3. The mirrors are adjusted so optimal conditions for lasing is achieved and the optical fibre is moved to the other waveguide, on the device to measure the absorbance of light passing through the absorbance cell. The absorption cell is filled with a buffer liquid and series of measurements are made by changing the pump power. The buffer solution in the absorbance cell is changed with a buffer solution containing Xylenol Orange and a new series of measurements are made. The light is analyzed using a fixed grating spectrometer (AVS-USB2000 from Avantes)

7.1.2 Issues

It is not possible to measure the power of the microfluidic dye laser, while simultaneously measuring the absorbance of light in the absorbance cell, as only one spectrometer is available. The drawback is that any fluctuations of the laser power are not taken into account and it may be difficult to compare measurements, thus any measured absorbance may be a combination of real absorbance of light and fluctuations of the emitted laser power. Therefore it is difficult to have an exact value for the absorption and all measurements must be carefully evaluated.

7.1.3 Setup B

In order to measure the emitted power from the microfluidic dye laser and simultaneously measure the absorbance in the absorbance detection cell, the use of photodiodes were intro-
(a) The chip holder with a chip. The directions of the in- and outlets are shown. The device holder is colored black in order to shield the device from the scattered laser light and avoid fluorescence.

(b) Optical image taken without 532 nm laser glasses. The laser beam is seen on the device and the circumference of the scattered light is seen. The laser light is scattered as the mirrors are not 100% perfect.

Figure 7.2: Optical image of the device holder and of the scattered laser light

Figure 7.3: Measurement setup with one waveguide. The device is placed in the device holder and pumped with the external pump laser and the optical fibre is placed in front of the waveguide using the adjustable tables.
The photodiodes (Hamamatsu, S1336-18B) were connected to an RC circuit, such that the charge generated in the photodiode is collected by the capacitor. The capacitor is slowly discharged through the resistance. By measuring the peak voltage on the capacitor, a value for the collected charge may be found, and therethrough a value for the emitted power from the device. It is required that the time constant of the RC-circuit is much larger than the pulse duration of the laser pulse [85]. The timescale of the RC-circuit is found to 1.2 $\mu$s, when $R=1$ k$\Omega$, $C=1.2$ nF, and the requirement is fulfilled. This method has several advantages, i) very little circuitry is involved ii) few steps are involved in the conversion of charge to a digital readout iii) the charge, and thereby the laser power may be integrated over a high number of laser pulses, in order to get good statistic on the measurements. The photodiodes where connected to a oscilloscope (54522A from Hewlett Packard) and the emitted power is measured as an average of 256 laser pulses.

Initially the photodiodes were glued onto the device using transparent glue. Two types of glue were tested, a silicone based glue (Glass silicone from Casco) and an epoxy based glue (Super Epoxy, type 3430 from Loctite). The two types of glue were different with respect to hardness after curing, as the silicone based was soft and flexible whereas the epoxy based was hard and brittle. The silicone based glue had the advantage, that the flexibility of the glue made it easy to mount the device in the device holder, and to work with the device in general, i.e. cleaning and storing. The drawback is that the wiring from the photodiodes would pull the photodiodes away from from the optimal position with respect to the waveguide on the device, i.e. 90°, and it would not be possible to compare different measurements if just a small change had been made, e.g. if one accidentally brushed the wires and thereby moved the photodiodes. The hard and brittle epoxy based glue did not have this drawback, as the photodiodes were held firmly in place, but the brittleness of the cured glue made it difficult to work with as the photodiodes would brake off if to much strain was imposed on the photodiode. This frequently happened while handling the device, or mounting it in the device holder. The approach with gluing the photodiodes on to the device was therefore abandoned. The photodiodes and circuitry were soldered onto a small piece of circuit board, and this board was aligned in front.
of the device, such that the photodiodes were placed in front of the waveguides on the device. The circuit board were held in place by the use of adhesive tape and a magnetic holder. This approach had the advantage that the photodiodes were held firmly in place, and that the handling of the device was very easy. The setup is shown in Fig. 7.4. When the photodiodes have been placed in front of the device holder, an optical fibre is placed on the side of the device using an adjustable table, the fibre is able to pick up a weak laser signal, thus it is possible to detect if lasing takes place.

### 7.1.4 Issues

A frequent problem was saturation of the photodiodes, as the power of the micro cavity dye laser was simply too high. The solution to the problem was to move the photodiodes away from the edge of the device (approximately 1 cm). Only the photodiode that collected light from the waveguide, guiding light directly from the laser, experienced saturation, the photodiode that collected the light that had been through the absorbance cell never experienced saturation, as the intensity from this waveguide is smaller.

In Fig. 7.5 the voltage signal from an unsaturated and a saturated photodiode is compared, the unsaturated photodiode has the characteristic shape of a RC-circuit charging and discharging, whereas the saturated photodiode has a plateau, which makes it impossible to determine the maximum voltage across the capacitor, and thereby the power of the signal. It was not possible to detect any absorbing in the channel when measuring with photodiodes, not even when the channel was filled with black ink, at best small attenuations in the order of 3-4 % was observed, but they were not reproducible. Later experiments should show that the photodiode has been placed directly in the flare from the inlet of the microfluidic dye laser, and therefore no change in the measured signal was observed.
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![Laser spectra](image1)

(a) Measured laser spectra using Rhodamine 6G dissolved in Ethanol \(2 \times 10^{-2}\) as the active medium at different pump laser powers.

![Laser Power](image2)

(b) Laser Power vs the pump laser power for the spectra shown in Fig. 7.6(a). The power has been found by numerically integration of the output spectra between 550 and 590 nm.

Figure 7.6: Measured laser spectra and power curves.

7.2 Optical measurements

7.2.1 Characterization of micro cavity dye laser

The laser cavity was characterized using setup A. During the characterization the absorption cell was empty. The Rhodamine was dissolved in Ethanol in a \(2 \times 10^{-2}\) mol/L solution. An example of the obtained laser spectra is shown in Fig. 7.6(a) and the corresponding power curve in Fig. 7.6(b). The laser is seen to be highly multimode, which is due to the grooved sidewalls shown in Fig. 6.12(b), a microfluidic dye laser with completely smooth sidewalls is expected to be more single mode as demonstrated by Daniel Nilsson [76]. The lasing threshold is found at 80 \(\mu\)J/mm\(^2\), but the threshold for lasing may vary from experiment to experiment depending on the alignment of the incoming pump laser beam. Thresholds as low as 65 \(\mu\)J/mm\(^2\) was observed, and this has also been reported for an identical microfluidic dye laser with completely smooth sidewalls [76]. Part of the initial investigations was to measure the intensity along the side of the device using the optical fibre in setup A. The position of the fibre was controlled by the adjustable table. In Fig. 7.7 the intensity of the pump laser light and the emitted laser light, are shown as a function of position along the device. It is seen that the light exits the device at the designated waveguides, hence position two and four. A small signal is detected at the same position as the pump laser light, position 3, and if one examines the laser spectra one can clearly see that it is not lasing, but could be either fluorescence or amplified spontaneous emission, which may originate from the inlets of the microfluidic dye laser. A relative large peak is observed at position 1 and it is interpreted as the residual layer is not small enough.
Figure 7.7: The light intensity measured along the side of the device. The signal is plotted for the emitted laser light and for the pump laser light. It is seen that the emitted laser light is guided by the waveguide as it exits the device at the designated positions. The pump laser light is not guided around the chip and is only observed at the position where the pump beam is focussed on the device. The outline of the device structures are shown for comparison.

to avoid guiding under the lens and therefore some light escapes that way. In general the light guidance around the chip seems to be demonstrated. The spectra in output spectra at the two waveguides are compared in Fig. 7.8 and it is seen that the signal is not changed significantly while travelling around the device. The most notable difference is the difference in intensity of the two signals.

7.2.2 Preliminary results for absorption measurements

The results presented in this section are measured on the same device using setup A. It has not been possible to reproduce the results using another device, when using either setup A or B. During the experiments the laser dye was pumped through the microfluidic dye laser with a pump rate of 50 μL/h. The buffer solutions for the absorption cell was changed manually. The optical fibre is aligned to the waveguide in order to maximize the amount of collected laser light. The output power is found by numerically integration over each measure spectra, and plotted as a function of pump laser power. This is done for the two experiments and shown in Fig. 7.9(a) and Fig. 7.9(b), where the measured power vs. pump power, is shown for two different buffer solutions in the absorbance cell. For Fig. 7.9(a) the lasing threshold is around 70-75 μJ/mm². The best linear fit for the sloped section of the power curve has been fitted for the two measurements series and the theoretical value for an absorption of 25 % of the light in the absorbance cell has been calculated on the basis of the best fit for the pure buffer solution. Based on other experiments the absorbance of these solutions in an absorbance cell of the length fabricated in this project, should be around 25-30 %. In Fig. 7.9(b) the measured laser power does increase much for high pump laser powers and when inspecting the spectra there is no evidence of why the increase takes place. The threshold is higher than the previous measurement and is found to 85μJ/mm². The measurements shown in Fig. 7.9 both have data
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Figure 7.8: Comparison of spectra from the two waveguides. The laser output is measured at position 2 in Fig. 7.7 and the signal output is measured at position 4 in Fig. 7.7. Notice the difference in intensity of the two signals.

(a) Absorbance measurements using different solutions of xylene orange in an ammonium buffer. (b) Absorbance measurements using different solutions of xylene orange in an ammonium buffer.

Figure 7.9: Absorbance measurements using the LOC device.
points that does not fit with the straight line. The reason for the deviations are unknown, but fluctuations in the emitted laser signal or bubbles in the absorbance cell could be possible explanations. The measurements were made using setup A, and it is not possible to take fluctuations of the emitted laser signal into account when using this setup.

7.2.3 Scattering in Topas

In order to investigate the functionality of the Fresnel lens, the laser cavity on the device was filled with Rh6G dissolved in Ethylene Glycol in a $2 \times 10^{-2}$ mol/L solution. The surface of the chip, that surrounds the laser cavity and Fresnel lens, was colored black and it was placed under a microscope with a filter, thus only the emitted laser light is observed, when the device is pumped with an external pump laser. The idea was to detect the emitted laser light in the Topas through scattering, this should provide an image of the focussed beam, after the emitted light had travelled through the Fresnel lens. Images were taken at high and low pump power, thus it should be possible to filter out the background noise by a subsequent image analysis in Matlab. The idea is, that at low pumping power the laser does not emit laser light and only the background noise is detected, this image is then subtracted from the image taken at high pump power and a image of the light path should appear. However it was only possible to see the circumference of the Fresnel lens due to scattering at the air/Topas interface. The only clear conclusion that can be drawn from this experiment, is that scattering in Topas is very low. The decision to design a laser device for investigation of the Fresnel lens was taken after this experiment.

7.2.4 Laser resistance of Topas

In order to investigate how high intensities of laser light, Topas is able to withstand without degrading, a device was filled with Rh6G dissolved in Ethylene Glycol in a $2 \times 10^{-2}$ mol/L solution. The power of the pump laser beam was optimized by setting the attenuator such that the transmitted beam was as powerful as possible. The beam was focussed onto the device, which was mounted in the device holder as under normal operation, the output of the device was measured using setup A. Lasing was obtained at low pump power and the power of the pump laser beam was increased, while the output of the device was observed. The power of the pump laser was increased until the output of the device no longer increased for increasing pumping powers, but showed a breakdown, indicating that the laser cavity had been damaged. The power of the pump laser beam was decreased to see if it was possible to reestablish lasing in the device, this was not possible. The device was investigated under an optical microscope, and it was observed that the microfluidic walls inside the laser cavity had been damaged, Fig. 7.10 shows the damaged structures.

The results are interpreted such that the pump laser beam was operated, at so high intensities that the temperature inside the Topas structure at some places increased to above 250 °C, and the Topas degraded at these locations, thus destroying the operation of the entire laser cavity.

I suspect that the temperature must exceed 250 °C as it is at this temperature degradation of the Topas polymer was observed, when baking the Topas coated wafers after spin coating.
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The reason that the laser may operate normally until the breakdown has two explanations, first the boiling point of Ethylene Glycol is 198 °C and as heat is easier transported in Ethylene Glycol than in Topas, the temperature in the laser medium does not reach as high values as the Topas. Secondly the intensity of the laser beam is not constant across the beam, this combined with the poor heat transport in Topas, makes it possible for localized areas in the Topas structures to reach temperatures where Topas degrade. The pump laser power at the onset of degradation was 490 μJ/mm², thus Topas can be used for applications where quite high pumping intensities are required.

7.2.5 Influence of residual layer thickness

In order to investigate the influence of the residual layer, and in that context get information on where and in what direction the emitted laser light leaves the device, a device with a thick residual layer was placed on a piece of white paper on the adjustable table. The device is filled with Rh6G dissolved in Ethylene Glycol in a $2 \times 10^{-2}$ mol/L solution, and the surface of the device is colored black. The device is pumped with the external pump laser, and the result is photographed through a pair of laser glasses, in order to filter out the scattered light from the laser. The photograph is seen in Fig. 7.11(a) and the structures on the device are shown by the white outline and it is seen that light exits the device at much more places than indicated by Fig. 7.7. Several things are interesting on the image. First the poor light guidance at the corner where the microfluidic dye laser is located, which indicates that the residual layer underneath the Fresnel lens and the waveguide is very high, as much light is not guided. Secondly flares are observed from the inlets of the microfluidic dye laser. The position of the microfluidic dye laser, makes one of the flares to point directly towards the position of the photodiode in setup B, and the light from the flare drowns the signal from the waveguide.
(a) Device where the residual layer has not been removed. The laser light exits the device at many different places.

(b) Device where the residual layer has been removed with an oxygen plasma.

Figure 7.11: The influence of the residual layer is illustrated by operating two devices, with and without residual layer under similar conditions. The structures on the device is shown as a white outline.
CHAPTER 7. OPTICAL MEASUREMENTS

This is not the case when using setup A, where the optical fibre is placed very close to the edge of the device, thus the flare may not interfere with the measurement. Furthermore, the optical fibre may not be able to detect the flare, as the fibre is only able to detect light exiting the device (almost) perpendicular to the edge of the device.

The experiment is repeated with a device where the residual layer is completely removed. The result is shown in Fig. 7.11(b). Several things are different when compared to the image in Fig. 7.11(a), first the light is much more confined to the waveguide in the corner, where the microfluidic dye laser is placed, and the peak intensity of the light is right in front of the waveguide, secondly a sharp "edge" is observed at the waveguide from the absorbance cell, which indicates that the light is guided in the waveguide. It is not possible to observe a confinement of the light in front of the waveguide from the absorption detection cell, as the flare drowns the signal. Again the flares from the inlets of the microfluidic dye laser is seen, this time they are more dominant, which may be caused by the fact that the imprinted structures are a little damaged, during the removal of the residual layer. The difference between image Fig. 7.11(a) and Fig. 7.11(b) illustrates the importance of controlling the residual layer when imprinting optical elements, and light control in general on LOC devices.

7.3 Summary and discussion

In this project two measuring setups have been implemented in connection with the existing optical setup in the basement at MIC; a setup using an optical fibre and a setup using an optical fibre together with two photodiodes. The respective issues in each of the setups have been identified. The imprinted laser cavity has been characterized and is found to be highly multimode due to the grooved sidewalls. The microfluidic dye laser emits laser light between 575 and 590 nm and the threshold for lasing is found to be around 65-70 μJ/mm². The excellent optical properties of Topas has indirectly been demonstrated by showing that almost no scattering takes place in Topas, thus in order to investigate the functionality of the imprinted lenses other methods must be used, e.g., through fluorescence. The functionality of the absorbance cell is demonstrated by operating the LOC with different buffer solutions in the absorbance cell. Unfortunately it has only been possible to reproduce the measurements on the same device using setup A. Attempts to reproduce the results using setup B was hampered by the fact that a flare from the inlet of the microfluidic dye laser drowned signal from the absorbance cell. The reason the flare was not observed when measuring the intensity of the emitted light along the edge of the device, with an optical fibre, is that the optical fibre may not be able to detect the flare, as the flare does not exit the device perpendicular to the edge of the device. Before setup B may be used with success, the LOC needs to be redesigned, such that the inlets of the microfluidic dye laser does not point towards the position of the photodiodes. Light control and the importance of controlling the residual layer, is demonstrated by operating two devices, one with a thick residual layer and one without residual layer.
Chapter 8

Conclusion and outlook

8.1 Conclusion

In this thesis, a technology for fabrication of Lab-On-a-Chip (LOC) microsystems, by Nanoimprint Lithography (NIL) in Topas is presented. The work involves investigations into imprinting in high $T_g$ Topas grades, so it is possible to fabricate devices in a high $T_g$ Topas grade and seal the imprinted structures with a low $T_g$ Topas grade. As part of this work it became clear that improvements to the anti-sticking coating had to be made, in order to be able to imprint in high $T_g$ Topas grades, such as 5013. Therefore investigations of the durability of different anti-sticking coatings was initiated, and it has been experimentally shown, that the C$_4$F$_8$ based anti-sticking coating previously used at MIC, is not capable of imprinting in Topas grade 5013. A commercial available anti-sticking coating based on fluorocarbon chains attached to a silane head group has been tested and has proven to be superior with regards to durability, release from the polymer film and is furthermore able to imprint in Topas grade 5013 and 6013. As a results of these investigations, a homebuilt anti-sticking coating chamber has been designed and constructed. The chamber is designed to control atmosphere and pressure during vapor phase deposition of fluorocarbon chains grafted to a silane head group. Initial experiments using stamps coated in the homemade chamber for anti-sticking coatings are promising and in the near future a process optimization will take place.

An integrated LOC device has been designed and fabricated, the LOC demonstrates an approach for integration of an on-chip light source with optical elements using 2D planar optics. The light source is a microfluidic dye laser, which emits laser light in the chip plane. The laser cavity has been developed by Søren Balslev and adapted for this thesis, and it is integrated with an absorbance detection cell by the use of a 2D planar Fresnel lens, which focusses the emitted light directly into a waveguide. The laser has been characterized and emits laser light between 576 and 590 nm, thus it is highly multimode. The lasing threshold has been found to 70-75 $\mu$J/mm$^2$. The functionality of the absorbance cell is demonstrated by operating the device with different solutions of Xylenol Orange in an ammonium buffer in the absorbance cell.

The importance of controlling the thickness of the residual layer has been demonstrated by operating two LOC devices, one with a thick residual layer and one where it has been removed.
CHAPTER 8. CONCLUSION AND OUTLOOK

Figure 8.1: Device for absorption and fluorescence detection on Carbon nanotubes. The device is made of two layers, a gold layer which is deposited on the substrate prior to imprinting (the blue layer) and a polymer layer with the microfluidic network embedded in it. The device has two detection points one at the end of the ingoing waveguide for fluorescence measurements and one in the center of the gold square where a small hole allows for the measured light to reach the detector. The gold layer shields the detector from stray light. A chip number is also incorporated in the gold layer.

It is shown that the light is much better confined in the device without residual layer, when compared to the other device, where the light escapes the designated light path through the residual layer.

Investigation have also been made into the limitations and advantages of using Topas. The scattering in Topas is presumably very low, as it was not detectable, the Topas device may also be pumped with pulsed laser beams at 532 nm, up to an effect of 490 $\mu$J/mm$^2$ without damaging the imprinted structures. Furthermore Topas’s vulnerability to Environmental Stress Cracking (ESC) have been identified and investigated. It was found that high $T_g$ grades of Topas experience ESC when exposed to Ethanol, Iso-Propanol and photoresist for a short time (seconds). ESC was also experienced for Topas grade 8007 when exposed to Ethanol for long periods (+6 hours). ESC is caused by induced stress, which is due to the thermal mismatch between Topas and the silicon substrate.

In order to investigate and compare the functionality of Fresnel and conventional lenses respectively, two devices have been designed and fabricated, but due to adhesion problems with the first (and only) batch no measurements have been made.

8.2 Outlook

The technology for fabrication of all Topas devices, which has been matured in this project, may be used for a wide range of applications, where the good optical and chemical properties of Topas may be exploited. In collaboration with the Nanointegration group at MIC, a device has been designed for fluorescence and absorption measurements on carbon nanotubes (CNT)
in a fluidic microchannel imprinted in Topas. The device is seen in Fig. 8.1 and consist of a
gold layer (blue) and a Topas layer with microfluidics (red), which are embedded between two
glass substrates. The device has two detection points, one at the end of the ingoing waveguide
for fluorescence measurements, and one in the center of the gold square for absorbance
measurements. The gold layer is made to shield the detector from light that has not passed
through the microfluidic channel.

This requires some alignment between the gold layer and the imprinted microfluidic net-
work. In practice this is done by patterning the gold layer, spin coat a Topas layer on top of it,
and aligning the patterned stamp to the gold substrate prior to imprint. This will be the first
attempt to align a stamp with predefined structures on a substrate at MIC, thus exploiting
the possibilities of the EVG 520EH imprinter. An important obstacle for fully exploiting the
wide range of Topas grades is ESC, that takes place in high $T_g$ grades when exposed to certain
liquid environments. In order to reduce the ESC one needs to remove the stress, which is
induced due to thermal mismatch between the Topas layer and the silicon substrate. When
silicon is used for stamp and substrate, LOC devices that are exposed to liquids are limited
to Topas grade 8007 and 9506. However devices that are not in contact with liquids may be
fabricated using high $T_g$ Topas grades.

The results obtained with the LOC device have shown that in order to use photodiodes
as detectors, a redesign of the device is required, so that 1) the inlets to the microfluidic dye
laser does not point towards the detectors, and 2) the laser cavity is turned in the horizontal
or vertical direction, so completely smooth side walls may be obtained. Making the sidewalls
completely smooth may also make the laser more single mode, than what have been achieved
here. Furthermore it is necessary to control the thickness of the residual layer and two ap-
proaches are available. The first one is to achieve better control with the initial thickness of
the polymer layer. This requires an optimization of the solvents used to dissolve the Topas
pellets, and such investigations are currently underway [80]. Secondly one may optimize the
Reactive Ion Etch used to remove the residual layer, so that it is possible to remove thick
residual layers without damaging the imprinted structures. In order to control the fluores-
cence from the waveguide one may introduce an extra fluidic channel around the inlet for the
microfluidic dye laser. This channel is filled with black ink, and the ink will absorb all emitted
light from the inlets. Such a proposal is seen in Fig. 8.2. The addition of such a fluidic network
to block fluorescent light, does not need to increase the complexity of the device holder, as the
surrounding channels may be filled with ink, before the device is mounted, thus removing the
need for extra inlets in the device holder.
Figure 8.2: Design proposal for a microfluidic dye laser, where the inlets (Red) are surrounded by ink filled microchannels (black), that absorb the emitted fluorescence from the inlets. The emitted laser light is illustrated with two green arrows pointing away from the laser cavity.
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Appendix A

Processing

A.1 Process sequence for stamp

1. Spin on photoresist
   - 30 s. HF buffer followed by 4 min in DI-water
   - A 1.5 μm thick layer of AZ5214E photoresist is spun onto the wafer
   - SSI spinner, track 1 using standard recipe PR1_5

2. Lithography
   - Exposure KS-Aligner (Karl Suss MA6/BA6)
     - Hard Contact
     - Exposure time 12 s
     - Constant Intensity

3. Development
   - The photoresist is developed in AZ51B developer for 1 min.
   - Followed by a 4 min rinse in DI-water and spin drying

4. ASE
   - Helium cooling of the backside during etch
   - ASE temperature is set to 10 °C
   - Etch time: 2.6 s, passivation time: 2.0 s

<table>
<thead>
<tr>
<th>Etch</th>
<th>Passivation</th>
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<tbody>
<tr>
<td>Coil</td>
<td>2800 W</td>
</tr>
<tr>
<td>Platen</td>
<td>16 W</td>
</tr>
<tr>
<td>SF₆</td>
<td>260 sccm</td>
</tr>
<tr>
<td>O₂</td>
<td>26 sccm</td>
</tr>
<tr>
<td>C₄F₈</td>
<td>120 sccm</td>
</tr>
</tbody>
</table>

- 56 cycles gives an etch depth of 10μm.
5. Removal of resist
- 2 min in the rough acetone
- 3 min in the fine acetone, with ultrasound
- 4 min in DI-water, then spin dry

6. Oxide growth
- Standard RCA cleaning procedure ([78])
- "Phospher drive in" oven
- Wet1000 for 90 min, gives a 450 nm thick oxide layer
- The thickness of the oxide is measured with the ellipsometer

7. Removal of Oxide in HF-buffer
- 8 min in HF-buffer
- 1 min water without N₂ bobbles
- 4 min with N₂ bobbles, then spin dry

8. Anti-sticking coating
- An anti-sticking coating is applied in the ASE, using a C₄F₈ gas.
- Backside cooling with helium
- C₄F₈ based coating
  - Oxygen plasma for 3 min, deposition of anti-sticking for 30 s.
  
<table>
<thead>
<tr>
<th>Oxygen plasma</th>
<th>Anti-sticking</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coil 800 W</td>
<td>Coil 300 W</td>
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<tr>
<td>Platen 20 W</td>
<td>Platen 20 W</td>
</tr>
<tr>
<td>O₂ 45 sccm</td>
<td>C₄F₈ 120 sccm</td>
</tr>
</tbody>
</table>

- Vapor phase deposition of silane-based anti-sticking coating
  - See Appendix C for a detailed description
A.2 Imprint process

1. Spin on Topas
   - For every new bottle of Topas in Toluene that has been mixed, a test wafer was made in order to check the thickness of the spun on layer of Topas.
   - The substrate wafer is prebaked at 150 °C for 10 min on a hotplate.
   - The Topas/Toluene solution is spun onto a wafer, 2000 rpm for 60 s, using the Speedline manual spinner.
   - The Topas/Toluene solution is applied with a pipette, which is cleaned with Ethanol and dried before use, and thrown away after a single use.
   - The Toluene is baked out at a hotplate at 150 °C for 10 min.

2. Imprint preparation
   - Stamp and substrate is blow dried prior to imprint using an N₂ gun.
   - The stamp and substrate placed face to face in the imprint machine.
   - Imprint chamber is evacuated to below 1×10⁻² mbar.

3. Imprint
   - The stamp and substrate are heated to 200 °C
   - The wafers are pressed together for 5 min.

\[
\begin{array}{|c|c|c|}
\hline
\text{Thyra} & \text{EVG 520EH} \\
\hline
\text{Force/wafer} & 4000 \text{ N} & 15000 \text{ N} \\
\hline
\end{array}
\]

4. Separation
   - The stamp and substrate is removed from the imprint machine when the temperature is below the \( T_g \) of the Topas grade
   - The stamp and substrate is rapidly cooled to room temperature by placing them on a metal table
   - A scalpel is gently pressed between the stamp and substrate and used to separate the wafers
5. Removal of residual layer

- Reactive Ion Etch
- Process is repeated in 30 s durations until the residual layer is completely removed.

<p>| | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>O₂</td>
<td>99 sccm</td>
<td>N₂</td>
<td>20 sccm</td>
</tr>
<tr>
<td>Pressure</td>
<td>300 mTorr</td>
<td>Cell power</td>
<td>100 W</td>
</tr>
</tbody>
</table>

A.3 Bonding

1. Cleaning of Pyrex glass lid

- 10 min cleaning in DI-water and Triton X100 soap under US aggregation
- 7UP etch (sulphuric acid and ammoniumperoxodisulphate at 80 °C for 10 min followed by 4 min in DI-water
- Spin dried

2. Spin on Topas

- The substrate wafer is prebaked at 150 °C for 10 min on a hotplate.
- The Topas/Toluene solution is spun onto the Pyrex wafer, 6000 rpm for 60 s. Speedline manual spinner.
- The Toluene is baked out at a hotplate at 150 °C for 10 min.
- A 10 μm thick protective layer of AZ4562 photoresist is spun on using the recipe az4562_10 on the KS spinner
- The photoresist is soft baked at 60 °C for 20 min on a hotplate.

3. Pattern definition

- The backside of the wafer is covered with adhesive tape.
- The adhesive tape on the backside is patterned using a CO₂ laser
- A similar pattern is patterned in a piece of adhesive tape, that after the patterning is placed on the frontside of the substrate, such that the patterns are aligned.
APPENDIX A. PROCESSING

4. Sandblasting

- The inlet holes are blasted through the pattern in the adhesive tape using 90 µm large Aluminum oxide particles using a sandblaster handpiece (Microetcher from Danville).
- Each holes takes approximately 10-15 s. to fabricate.

5. Cleaning of sandblasted substrates

- The substrates are rinsed in DI-water using a water gun, then the adhesive film is removed.
- The Substrates are rinsed in DI-water+N₂ bubbles for 5 min.
- The protective layer of photoresist is removed in Acetone and the substrates are rinsed in DI-water for 4 min.

6. Bonding

- Pyrex glass lid and imprinted structures are flushed with Isopropanol(IPA) and blow dried using a N₂ gun.
- Pyrex glass lid and imprinted structures are placed face to face in the imprint machine.

<table>
<thead>
<tr>
<th>Thyra</th>
<th>EVG 520EH</th>
</tr>
</thead>
<tbody>
<tr>
<td>Force/wafer</td>
<td>4000 N</td>
</tr>
<tr>
<td>Temperature</td>
<td>65 °C</td>
</tr>
</tbody>
</table>

- They are pressed together for 5 min and then cooled to 45 °C.
Appendix B

Diagram of chamber for VPD
APPENDIX B. DIAGRAM OF CHAMBER FOR VPD

Figure B.1: Diagram of chamber for VPD, the numbering on the diagram is similar to the numbering shown in Fig. 3.8. 2 Valves for Argon and Nitrogen. 3 Regulator, operates both valves, such that only one gas may be flushed through the chamber at once. 5 Chamber. 6 Pressure gauge. 7 Septum. 8 Valve to pump. 9 Dirt collector. 10 Membrane pump.
Appendix C

Manual for the anti-stiction chamber

C.1 Pretreatment

- HF-buffer for 30 s
- DI-water + N₂ bobbles for 4 min
- Oxygen plasma for 3 min
  - power (coil) = 800 W ± 5 %, power (plate) = 20 W ± 5 %
  - Oxygen = 45 Sccm ± 5 %
  - Pressure = 45 mTorr ± 10 %
  - Helium backside cooling = on

C.2 Coating

- Place stamp in chamber
- Turn on pressure gauge and membrane pump on the switch’s on the top of the machine
- Open the pump valve (located under the chamber) and pump down to P < 3 mbar.
- Close pump valve
- Switch to Argon on the middle switch, and flush with Argon until P > 100 mbar
- Open pump valve and pump down to P < 3 mbar
- Close pump valve and flush with Argon until P ~ 10 mbar
- Fill syringe with 5 µL of silane solution
- Clean the needle and punch through the septum
APPENDIX C. MANUAL FOR THE ANTI-STICKTION CHAMBER

• Slowly inject the silane. The injection should take about two minutes. When finished leave the syringe in the septum.

• Start a timer and wait 10 min.

• Flush with Argon till P > 750 mbar

• Open pump valve and pump down to P < 10 mbar.

• Close pump valve, and switch main switch to Nitrogen

• Flush with Nitrogen till P > 1000 mbar, when the pressure reaches 900 mbar, the handle on the hatch is pulled, thus no overpressure in the chamber is possible.

• Remove stamp

• Pull out syringe and clean the needle and the piston in the syringe, thus they do not corrode. They are cleaned by wiping them with a cleanroom tissue.

• Leave the anti-stiction chamber in a dry Nitrogen atmosphere at ~1000 mbar.
Appendix D

Chip and wafer layout
Figure D.1: The stamp layout for the LOC for absorbance measurements. The outer ring shows the outline of a wafer and the inner ring shows the outline of the PDMS matters initially used as cushion between the stamp and the chuck.
Figure D.2: The stamp layout for the lasers for lens investigations. The outer ring shows the outline of a wafer and the inner ring shows the outline of the PDMS matters initially used as cushion between the stamp and the chuck.
APPENDIX D. CHIP AND WAFER LAYOUT
Appendix E

Sketch of the Fresnel lens
Figure E.1: Sketch of the Fresnel lens, the image is exported from L-Edit, which is why the edge of the lens look so rugged. Only the left half of the lens is shown, as the lens is symmetrical around the center of the lens. The width of the different parts of the lens is indicated, and the lateral position of the saw teeth.
Appendix F

Conference proceedings: Eurosensors 2005

The results from the work made in this thesis with regards to the integrated Lab-On-a-Chip microsystem is accepted for an oral presentation at the 19th European Conference on Solid-state transducers, Eurosensors XIX, Spain, September 11th-14th 2005. The paper that is going to be presented is reprinted in the following four pages.
A POLYMER LAB-ON-A-CHIP WITH INTEGRATED OPTICS FABRICATED BY NANOIMPRINT LITHOGRAPHY

Michael Hansen, Søren Balslev and Anders Kristensen*

MIC – Department of Micro and Nanotechnology, Technical University of Denmark, Oersteds Plads, Building 345 east, 2800 Kongens Lyngby, Denmark

* email: ak@mic.dtu.dk, phone: +45 4525 6331, fax: +45 4588 7762

Abstract: In this paper we present a Lab-on-a-chip (LOC) with integrated microfluidics and planar optics, fabricated by nanoimprint lithography (NIL) in a cyclic-olefin-copolymer, Topas. The LOC contains a microfluidic network, an absorbance cell, optical waveguides, a microfluidic dye laser and Fresnel lenses that couples the light into the waveguides. Rhodamine 6G dissolved in ethylene glycol is used as the active laser medium and lasing is observed between 576 and 590 nm. Light control on the LOC by removing the residual layer is demonstrated and the LOC is operated with different solutions of Xylenol Orange in the absorption cell.

Keywords: Polymer Lab-on-a-chip, planar integrated optics, nanoimprint lithography

INTRODUCTION

The integration of optical elements on Lab-on-a-chip (LOC) Microsystems is an attractive approach, as optical techniques play a significant role in chemical and biological analysis [1]. LOC’s are preferably fabricated in polymers, in order to achieve a low cost system. Previously poly-methylmethathacrylate (PMMA) and the negative epoxy based photoresist SU-8 have been used to fabricate microfluidic networks combined with micro optics [2,3]. We use Topas® from Ticona [4], which is a highly transparent cyclic-olefin-copolymer, with excellent mechanical properties, thus optimal for nanoimprint lithography (NIL). Furthermore Topas® is highly chemical resistant towards polar solvents, acids and bases, has a low propagation loss at wavelengths above 300 nm, and it is biocompatible. Furthermore it has a low water uptake (<0.01%) compared to other polymers, e.g. PMMA (0.3%)

The glass transition temperature, Tg, of Topas can be tailored by changing the ratio between its two components, Norbornene and Ethylene. Topas is a promising material for fabrication of all polymer LOC devices, as the structures can be fabricated in a high Tg Topas grade, and sealed with a low Tg Topas grade.

In this paper we present the fabrication of a LOC device for absorbance measurements (see figure 1), with millimetre to micrometer sized structures in one lithographic step. The device is imprinted into a 10 µm thick layer of Topas 8007 which is spin coated onto a silicon wafer with a 3 µm thick thermally grown SiO2 layer, thus ensuring guidance of the light, due to the lower refractive index of SiO2 (n = 1.46) than for Topas (n=1.53). The microfluidic network, defined in Topas® grade 8007 is sealed off by thermal bonding of a Pyrex glass lid (n=1.50), using Topas® grade 9506 as a bonding layer. The device demonstrates an approach for collecting and focusing light from a large integrated light source [5] into a single waveguide by the use of Fresnel lenses.

In addition, the NIL approach allows for addition of nanometer-scale features, limited only by the stamp fabrication.

DESIGN

The laser structure is made up of an array of parallel microfluidic channels. The structure forms a distributed feedback resonator, which supports a number of longitudinal modes in the spectral gain range of the laser dye Rhodamine 6G. The laser resonator design is adapted from [6]. The laser cavity, fabricated in Topas, has been characterized elsewhere [5].

Fresnel lenses are placed on each side of the laser cavity, thus focussing the light into the waveguides, see figure 2. The Fresnel lenses are 1030 µm long, and have a focal length of 1500 µm. The width of the Fresnel lenses vary from 10 up to 75 µm. Along the in- and outlet of the laser, fluorescence blockers are placed, thus blocking some of the fluorescence that may be generated in the inlets during operation, when the microfluidic dye laser is pumped with an external pump laser. Fresnel lenses where chosen because they have a lower loss of light, than conventional lenses, see figure 3, and they take up less space on the chip, thus allowing for a smaller, more integrated chip.
Fig. 2. Scanning Electron Microscope image of the imprinted device. The light from the laser resonator is focussed directly into the waveguides by the two Fresnel lenses.

Fig. 3. The fresnel lens has a less anti guiding than a conventional lens, as seen in situation a) and c) at the end of the lenses. Whereas the center of the two lenses are the same, as seen in situation b) and d).

The fluidic network can be devided into two parts. The first one is the mixer, which leads to the absorption detection cell. It is made of three channels, which meet and form a mixer. The channels are 90 µm wide and 10 µm high. The lengths of the channels are 7.5 mm.

The second is leading away from the absorbance cell. The channel leading away from the absorbance cell are initially 90 µm wide, but over a 200 µm distance it widens to 180 µm, from here it is 5.7 mm long. The inlet and outlets are 2.5 mm in diameter. The absorbance cell is 260 µm long, 90 µm wide and 10 µm high, see figure 4. The waveguide leading light into the absorbance cell is tapered, thus ensuring a more collimated light beam [7]. At the end of the absorbance cell, a conventional lens is placed, the lens is 170 µm long and has a focal length of 1500 µm and focuses the light into the waveguide.

Fig. 4. Optical image of the absorbance detection cell. The ingoing waveguide is tapered to keep the light collimated, and a small lens focuses the light into the outgoing waveguide.

FABRICATION

The silicon stamp for the imprint process is fabricated by standard UV-lithography and silicon deep reactive ion etching (DRIE). The sidewall roughness of the DRIE process is reduced to below 15 nm by thermal oxidation and subsequent oxide etching [5]. Prior to imprint the stamp is coated with an anti-sticking coating from a perfluorodecyltrichlorosilane precursor by molecular vapor deposition [8].

Topas®, in our case grade 8007 (T_g=75°C), dissolved in a 23 wt% solution in toluene, is spin coated onto a SiO_2 substrate. Prior to spin coating the SiO_2 substrates are dehydrated on a hotplate at 150°C for 10 min.

The imprint is made in an EVG 520HE nanoimprinter [9]. The imprint temperature is 200 °C, which is well above the glass transition temperature. The imprint force is 15000 N on a 4 inch wafer, imprint time is 5 min. To ensure a homogenous imprint two 0.5 mm thick graphite sheets are used on the chucks of the nanoimprinter.

The residual layer is removed with oxygen plasma in a Reactive Ion Etching (RIE) tool. The RIE process is applied for 30 s, and the substrate is cooled before the process is repeated. The cycle is repeated until the residual layer is removed. The cyclic process ensure that the imprinted structures remain intact. A continuous etch would heat the substrate and reflow of the Topas would occur, thus rendering the imprinted structures useless.

The imprinted structure is sealed with a Pyrex glass lid, with a second layer of Topas® in our case grade 9506 (T_g=65°C) as intermediate layer. The bonding layer is 200 nm thick. Prior to spin coating the pyrex glass wafer is cleaned with X100 detergent under US-aggregation for 10 min and a 7-UP etch (sulphuric acid and ammoniumperdisulfate at 80 °C). Immediately before spin coating the glass wafer is baked at 150 °C for 10 min, thus dehydrating the surface. The spin coating is followed by a 10 min bake at 150 °C. The bonding is performed in the imprint machine and the bonding temperature is 70 °C, at a bonding force of 5000 N on a 4 inch wafer. Bonding time is 5 min. Details on NIL in Topas are given in [10].
EXPERIMENTAL SETUP
Solutions of Rhodamine 6G dissolved in ethanol or ethylene glycol are prepared, both with a concentration of 2·10^{-2} mol/L. The solutions are pumped through the chip with a flow rate of 50 µL/hr to avoid bleaching of the Rhodamine. The dye is optically pumped through the Pyrex glass lid with a pulsed (10 Hz, 5 ns duration), frequency doubled Nd:YAG laser (Continuum Surelite I-10) emitting at 532 nm. The microfluidic dye laser emits light in the chip plane, which is focussed into the waveguide by the Fresnel lens and guided to the edge of the chip, where an optical fibre collects it. The light is analyzed by a fixed grating spectrometer (AVS-USB2000 from Avantes). To avoid fluorescence signals from the in and outlet, the area around the laser cavity and the chip holder is coloured black. The active laser medium is pumped with an external syringe pump (Harvard 11Plus). The samples to be analyzed are manually pumped through the device, by a syringe.

RESULTS
The integrated microfluidic dye laser emits laser light at wavelengths between 576 nm and 590 nm, (see figure 5). The lasing threshold is found to be 75 µJ/mm².

The emitted laser light is focussed at the outputs of the device and the two output signals from the device are compared to confirm that the laser signal is guided around the chip. The intensity at the signal output is lower due to losses in the absorbance detection cell. The importance of removing the residual layer is shown in figure 6. Here two chips are placed on a piece of white paper and the lid around the laser cavity is coloured black. The laser cavity is pumped, and the guidance of light around the entire chip is shown at the edges. The first situation is a chip with a residual layer, and the poor guidance is seen in figure 6A. The residual layer allows the light to escape the designated light path, thus rendering the chip useless due to poor light control. The second situation, figure 6B, is a chip where the residual layer is removed. The guidance of light is much better, and very little light exits the designated light path. A higher fluorescence is observed, as the laser cavity is slightly damaged during the RIE etch, this is seen as an increased intensity from the fluorescence blockers.

![Fig. 5.](image)

**Fig. 5.** The output spectra from the device, when the microfluidic dye laser is pumped by a frequency doubled Nd:YAG laser at 53 nm, at a pump power of 281 µJ/mm². The laser is multimode and is emitting laser light between 576 nm and 590 nm. The laser output and the signal output correspond to position 2 and 4 in Fig. 6 respectively.

![Fig. 6.](image)

**Fig. 6.** A) A chip with the residual layer is pumped and the guidance of light in the residual layer is shown, as light exits the chip at many locations. B) The residual layer has been removed, and better guidance of light is observed. An increase in fluorescence from the laser is observed, as the laser cavity is slightly damaged by the Reactive Ion Etching of the residual layer. The structures on the chip are shown as a white outline.

The guiding of the light through the device is illustrated in figure 7, where the intensity of the light is shown as a function of position along the edge of the chip.

Different concentrations of Xylenol Orange, in an ammonium buffer, are used in the absorbance detection cell (see figure 8) and the functionality of the absorbance cell is demonstrated. During operation it was observed that the Rhodamine/ethanol solution gives rise to Environmental Stress Cracking in the polymer structures. These cracks allowed access for the solution to the Fresnel lenses, thus destroying the
functionality of the lens. Such effects were not observed for the Rhodamine/Ethylene glycol solutions.

Fig 7. The intensity along the side of the chip are shown for the pump laser and the microfluidic dye laser and compared to the layout of the chip. This shows that the light is guided in the waveguides.

Fig. 8. The output power of the absorbance detection cell is measured for two different solutions of Xylenol Orange in an ammonium buffer. In theory a 0.06 mM solution should absorb approximately 25% of the light, which matches with the experimental results. The laser threshold is 75 µJ/mm².

CONCLUSION
We have successfully demonstrated the fabrication and integration of optical elements on a LOC fabricated by NIL and wafer bonding in Topas®. The importance of removing the residual layer when imprinting optical elements has been demonstrated.

As shown in figure 5, the Fresnel lenses are capable of focusing the emitted laser light into the waveguides, thus controlling the light path. The functionality of the absorbance detection cell has been demonstrated by filling the absorbance cell with different solutions of Xylenol Orange during operation.

ACKNOWLEDGEMENTS
We thank Jörg Kutter for supplying the ammonium buffer and the Xylenol orange solutions.

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9. EVG 520HE nanoimprinter by EV Group, Schärding, Austria
Appendix G

Conference proceedings: Optics and Photonics 2005

The results from the work made in this thesis with regards to the integrated Lab-On-a-Chip microsystem is accepted for an oral presentation at Optics and Photonics 2005, San Diego, USA, July 31st - August 4th 2005. The paper that is going to be presented is reprinted in the following seven pages.
A nanoimprinted polymer lab-on-a-chip with integrated optics

M. Hansen and D. Nilsson and D. M. Johansen and S. Balslev and A. Kristensen
MIC - Department of Micro and Nanotechnology, Technical University of Denmark (DTU), DK-2800 Kongens Lyngby, Denmark

ABSTRACT

We present a polymer lab-on-a-chip (LOC) microsystem with integrated optics, fabricated by thermal nanoimprint lithography (NIL) in a cyclic olefin copolymer, Topas from Ticona. The LOC contains microfluidic channels and mixers, an absorbance cell, optical waveguides, a microfluidic dye laser, and Fresnel lenses to couple light in and out of the waveguides. The polymer structure is embedded between two glass substrates. By this device we exploit the excellent chemical, mechanical and optical properties of Topas, and demonstrate the fabrication of millimeter to micrometer sized structures in one lithographic step. In addition, the NIL approach allows for addition of nanometer-scale features, limited only by the stamp fabrication. The silicon stamp for the imprint process is fabricated by standard UV-lithography and silicon deep reactive ion etching (DRIE). The sidewall roughness of the DRIE process is reduced to below 15 nm by thermal oxidation and subsequent oxide etching. Prior to imprint the stamp is coated with an anti-sticking coating from a perfluorodecyltrichlorosilane precursor by molecular vapor deposition. Topas, in our case grade 8007, dissolved in toluene is spin coated onto a SiO$_2$ substrate. The imprint temperature is 200 °C, at an imprint force of 15000 N on a 4 inch wafer, imprint time is 5 min. Finally the imprinted structure is bonded to a pyrex wafer with a second layer of Topas in our case grade 9506. Bonding temperature is 70 °C, at a bonding force of 5000 N on a 4 inch wafer. Bonding time is 5 min.

Keywords: Polymer lab-on-a-chip, integrated optics, nanoimprint

1. INTRODUCTION

The introduction of optical elements on Lab-on-a-chip (LOC) devices is an attractive approach, as optical detection techniques play a significant role in chemical and biological analysis. LOC microdevices are preferable fabricated in polymers, as the fabrication cost for polymer devices is significantly lower than for silicon based devices. Previously poly-methylmethathacrylate (PMMA) and the negative epoxy based photoresist SU-8 have been used for the fabrication of Lab-on-a-Chip (LOC) devices with integrated optics. It should be noted that SU-8 was not developed for optical applications and therefore has a strongly increasing optical loss at wavelengths below 600 nm. Furthermore PMMA is not resistant towards many reagents commonly used in chemical analysis. Therefore it is attractive to replace these materials with other materials that matches or have better properties than SU-8 and PMMA. We presents the results obtained with the cyclic-olefin copolymer, Topas from Ticona.

Previously Topas has been demonstrated as a suitable material for nanoimprint lithography (NIL). Topas is attractive as it is highly resistant to polar solvents, acids and bases, has a low propagation loss at wavelengths above 300 nm, a refractive index of 1.53 and it is bio-compatible. Furthermore Topas has a low water uptake (< 0.01%) compared to other polymers, e.g. PMMA (0.3%).

Since Topas is a copolymer it is possible to tailor the glass transition temperature $T_g$, by changing the content of the Norbornene component between 60 wt.% and 85 wt.%, respectively. This makes it possible to fabricate device structures in a high $T_g$ Topas grade and seal the imprinted structures with a low $T_g$ Topas grade, thus creating an all polymer LOC device. The fabricated device is shown in Fig. 1.
Figure 1. Optical image of the fabricated device for absorbance measurements. The device contains a microfluidic dye laser, an absorbance detection cell, Fresnel lenses, planar waveguides and a microfluidic network.

2. DESIGN

The laser structure consists of an array of parallel microfluidic structures, forming a laterally emitting distributed feed-back resonator. The design is adapted from. The imprinted laser cavity has been characterized elsewhere. The structure supports a number of longitudinal modes in the spectral gain range of the laser dye, Rhodamine 6G. The laser resonator is shown in Fig. 2, which also shows the Fresnel lens used to focus the light into the waveguides, A Fresnel lens is placed on each side of the laser cavity. The Fresnel lenses are 1030 µm long, and the width of the lenses vary from 10 up to 75 µm. Fluorescence blockers are placed along the in and outlet of the laser cavity, in order to block any fluorescence that may be generated in the inlets while the device is pumped with the external pump laser. The Fresnel lenses were chosen to be implemented instead of conventional lenses as they take up less space on the device and they have a lower loss of light, this is illustrated in Fig. 3

The fluidic network can be divided into two parts. The first part is the mixer, which leads to the absorption detection cell. It is made of three channels, which meet and form a mixer. The channels are 90 µm wide and 10 µm high. The lengths of the channels are 7.5 mm. The second part is leading away from the absorbance cell. The channel leading away from the absorbance cell is initially 90 µm wide, but over a 200 µm distance it widens to 180 µm, from here it is 5.7 mm long. The inlet and outlets are 2.5 mm in diameter. The absorbance cell is 260 µm long, 90 µm wide and 10 µm high, see figure 4. The waveguide leading light into the absorbance cell is tapered, thus ensuring a more collimated light beam. At the end of the absorbance cell, a conventional lens is placed, the lens is 170 µm long and has a focal length of 1500 µm and focuses the light into the waveguide.

3. FABRICATION

The silicon stamp for the imprint process is fabricated by standard UV-lithography and silicon deep reactive ion etching (DRIE). The sidewall roughness of the DRIE process is reduced to below 15 nm by thermal oxidation
Figure 2. SEM image of the imprinted laser resonator and Fresnel lens. The microfluidic channels in the laser resonator is 20 µm wide and 10 µm high.

Figure 3. Comparison of conventional and Fresnel lens. The Fresnel lens has less anti-guiding than the conventional lens, as seen in situation a) and c) at the end of the lenses. At the center of the lenses the situation are the same, as seen in b) and d)
Figure 4. Optical image of the absorbance detection cell. The liquid to be analyzed flows through the absorbance cell during measurements. The incoming waveguide is tapered to ensure a more collimated light beam inside the absorbance cell. A small conventional lens focuses the light into the outgoing waveguide.

and subsequent oxide etching. Prior to imprint the stamp is coated with an anti-sticking coating from a perfluorodecytrichlorosilane precursor by molecular vapor deposition.

Topas, in our case grade 8007 (Tg=75 °C), dissolved in a 23 wt% solution in toluene, is spin coated onto a SiO₂ substrate. Prior to spin coating the SiO₂ substrates are dehydrated on a hotplate at 150 °C for 10 min. The imprint is performed with an EVG 520HE parallel plate nanoimprinter. The imprint temperature is 200 °C, which is well above the glass transition temperature. The imprint force is 15000 N on a 4 inch wafer, imprint time is 5 min. To ensure a homogenous imprint two 0.5 mm thick graphite sheets are used on the chucks of the nanoimprinter. The residual layer is removed with oxygen plasma in a Reactive Ion Etching (RIE) tool. The RIE process is applied for 30 s, and the substrate is cooled before the process is repeated. The cycle is repeated until the residual layer is removed. The cyclic process ensure that the imprinted structures remain intact. A continuous etch would heat the substrate and reflow of the Topas would occur, thus rendering the imprinted structures useless.

The imprinted structure is sealed with a Pyrex glass lid, with a second layer of Topas in our case grade 9506 (Tg=65 °C) as intermediate layer. The bonding layer is 200 nm thick. Prior to spin coating the pyrex glass wafer is cleaned with X100 detergent under ultra-sonic aggregation for 10 min and a 7-UP etch (sulphuric acid and ammoniumperdisulfate at 80 °C). Immediately before spin coating the glass wafer is baked at 150 °C for 10 min, thus dehydrating the surface. The spin coating is followed by a 10 min bake at 150 °C. The bonding is performed in the imprint machine and the bonding temperature is 70 °C, at a bonding force of 5000 N on a 4 inch wafer. Bonding time is 5 min. Details on NIL in Topas are given in.

4. EXPERIMENTAL SETUP

Rhodamine 6G is dissolved in Ethylene Glycol in a 2×10⁻² mol/L concentration. The solution is pumped through the laser cavity with a flow rate of 50 μL/hr in order to avoid bleaching of the laser dye. The laser dye is pumped with an external syringe pump (Harvard 11Plus). The laser cavity is optically pumped through the Pyrex glass lid with a pulsed (10 Hz, 5 ns duration) frequency doubled Nd:YAG laser (Continuum Surelrite I-10) emitting at 532 nm. The laser cavity emits laser light in the chip plane, where it is focussed into the waveguides by the Fresnel lenses. The light is collected at the edge of the device by an optical fibre and analyzed using a
Figure 5. The output from the two waveguides when the microfluidic dye laser is pumped with a frequency doubled Nd:YAG laser at 532 nm, at a pump power of 281 µJ/mm². The laser is seen to be multimode and emitting laser light between 576 nm and 590 nm. The two output spectra are comparable, thus the emitted signal is not altered on its way through the device.

fixed grating spectrometer (AVS-USB2000 from Avantes). In order to avoid fluorescence from the in and outlets of the laser cavity, the Pyrex glass lid is colored black around the laser cavity, thus shielding the laser dye in the inlets from the pump laser light. The samples to be analyzed are pumped through the device manually by a syringe.

5. RESULTS

The emitted laser light is collected at the two output waveguides and compared, see Fig. 5 in order to ensure that the light is guided round the device and that the spectral signature of the signals are alike. The laser is observed to be highly multimode and emitting laser light between 576 nm and 590 nm. The intensity at the signal output is lower than the signal at the laser output, due to losses in the absorbance detection cell and a longer path length. The importance of controlling the residual layer is investigated by comparing how the light is emitted from a device with a high residual layer and a device where the residual layer has been removed. Two devices, one with a high residual layer and one without, are prepared by filling the laser cavities with Rhodamine 6G dissolved in Ethylene Glycol and the entire surface of the device, except the laser cavity, is colored black. The devices are placed on a white piece of paper, thus it will be possible to observe where and in what direction the light exits the device. In Fig. 6 A an optical image of the device is shown, while the device is being pumped with the external pump laser. The most striking thing is the poor light guidance at the corner where the microfluidic dye laser is located, which indicates that much light escapes the designated light paths due to the residual layer.

The experiment is repeated for a device where the residual layer has been removed. The result is shown in Fig. 6 B, and a much better guidance of light is observed especially at the waveguide in the corner where the microfluidic dye laser is placed, as the intensity of the light is confined in front of the waveguide. Furthermore a sharp ”edge” is observed at the waveguide coming from the absorbance cell, which indicates that the light is guided in the waveguide. The reason that a bright intensity spot is not observed in front of that waveguide is the ”flares” that are emitted from the in and outlets of the microfluidic dye laser. The flares comes from fluorescence.
in the inlets and laser cavity. The reason for the increase in fluorescence for the device where the residual layer has been removed is that the laser cavity may have been slightly damaged during the removal of the residual layer.

The functionality of the absorbance detection cell is demonstrated by using different solutions of Xylenol orange dissolved in an ammonium buffer in the absorbance cell. The transmitted light is measured for different pump laser powers and the Xylenol Orange solution is replaced and the experiment is repeated. According to previous experiments a 0.06 mM solution of Xylenol Orange should absorb approximately 25% of the light in an absorbance cell like the one presented in this paper. This fits well with the obtained results. The results are visualized in Fig. 7

6. CONCLUSION

In conclusion, we have successfully demonstrated the fabrication and integration of optical elements with a light source on a Lab-on-a-Chip (LOC) device. The LOC device is fabricated with nanoimprint lithography (NIL) and wafer bonded in Topas. The device have been imprinted in Topas grade 8007 ($T_g=75^\circ$C) and sealed with an intermediate layer of Topas grade 9506 ($T_g=65^\circ$C). This allows for a bonding temperature of 70, which ensures no reflow takes place in the imprinted structures.

Light control have been demonstrated by controlling the residual layer, which is removed by an oxygen plasma in a Reactive Ion Etch.

The functionality of the absorbance cell has been demonstrated by filling the absorbance cell with different solutions of Xylenol Orange during operation of the device.

ACKNOWLEDGMENTS

This work is supported by the Danish Technical Research Council (grant no. 26-02-0064). The partial support of the EC-funded project NaPa (Contract no. NMP4-CT-2003-500120) is gratefully acknowledged. The content of this work is the sole responsibility of the authors. We thank Prof. Jörg P. Kutter for supplying the ammonium buffer and the Xylenol orange solutions.
Figure 7. The output of the absorbance detection cell is measured, when the absorbance cell is filled with two different solutions of Xylenol Orange in an ammonium buffer. In theory a 0.06 mM solution should absorb approximately 25% of the light, which matches with the experimental results. The laser threshold is $85 \mu J/mm^2$.

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Appendix H

Journal Papers: Journal of Vacuum Science and Technology B

The work made in this thesis, with regards to the developing the technology platform, for making imprints in both low and high $T_g$ Topas grades is presented at the forty-ninth International Conference on Electron, Ion and Photon beam technology and Nanofabrication, Orlando, USA, May 31st - June 3rd, 2005. The conference proceeding is printed as a journal paper in: Journal of Vacuum Science and Technology B, and is due in 2005. The contribution is reprinted on the following pages.
Topas Based Lab-on-a-chip Microsystems Fabricated by Thermal Nanoimprint Lithography

B. Bilenberg†, M. Hansen†, D. Johansen†, V. Özkapıcı†, C. Jeppesen†, P. Szabo†, I. M. Obieta§, O. Arroyo§, J. O. Tegenfeldt¶ and A. Kristensen†

†MIC - Department of Micro and Nanotechnology, Technical University of Denmark (DTU), DK-2800 Kongens Lyngby, Denmark
‡Department of Chemical Engineering (KT), Technical University of Denmark (DTU), DK-2800 Kongens Lyngby, Denmark
§Inasmet-Tecnalia, 20009 San Sebastian, Spain
¶Division of Solid State Physics, Lund University, P. O. Box 118, SE-221 00 Lund, Sweden

(Dated: August 1, 2005)

Abstract

We present a one-step technology for fabrication of Topas based lab-on-a-chip (LOC) microsystems by the use of thermal nanoimprint lithography (NIL). The technology is demonstrated by the fabrication of two working devices: a particle separator and a LOC with integrated optics for absorbance measurements. These applications demonstrate the fabrication of millimeter to micrometer-sized structures in one lithographic step. The use of NIL makes the technology easily scalable into the nanometer-regime by the use of a suitable lithographic technique in the fabrication of the stamp. Processing issues such as environmental stress cracking of the Topas and the requirements to anti-sticking layers on the stamp when imprinting into Topas are discussed.
INTRODUCTION

The continuous refinement of lab-on-a-chip (LOC) systems in which microfluidics and passive and active optical elements are combined, requires new materials with superior properties regarding fluidic handling and optics [1–3]. The development of effective point of care LOC devices demands use-once-and-throw-out devices primarily fabricated in polymers to minimize fabrication costs and avoid environmental hazards. Previously, polymethylmethacrylate (PMMA) and the negative tone epoxy based photoresist SU-8 (MicroChem) has been used to fabricate microfluidics combined with microoptics [4, 5]. SU-8 is easily patterned by ultraviolet lithography (\(\lambda = 365\) nm) and is a suitable material for microfluidics but is not optimal for highly effective passive and active optical elements due to its high propagation loss in the visible region [6, 7].

We present the results obtained with the random cyclic-olefin-copolymer, Topas [8], consisting of a mixture of ethylene and norbornene. Previously Topas has been demonstrated to be a suitable material for nanoimprint lithography (NIL) [9]. Recently, cyclic olefin polymers and copolymers have received attention as promising materials for LOC [10] because of their optical transparency and chemical stability. Topas is highly resistant to polar solvents, acids and bases, it has a high water vapor barrier, a low propagation loss at wavelengths above 300 nm, a refractive index of 1.53 and it is bio-compatible. Since Topas is a copolymer some of its physical properties can be tailored by changing the proportions of its two components. The glass transition temperature, \(T_g\), of the material can be tailored between 65°C and 180°C by changing the content of the norbornene component between 60 wt.% and 85 wt.%, respectively. Thus, Topas is a potential material for the fabrication of all polymer LOC devices, and the device structure can be fabricated in a high-\(T_g\) Topas grade by NIL while the device can be sealed with a low-\(T_g\) Topas grade. In this paper we present the results obtained with the fabrication of devices in Topas grades 8007 and 5013, sealed with Topas grade 9506. The glass transition temperatures and the viscosities are tabulated in Table III.

The capabilities of the Topas technology platform is demonstrated by two working devices. A particle separator, see Figure 1, adapted from Huang et al. [11], which demonstrates the possibility of making high aspect ratio structures in Topas and a LOC for absorbance measurements on a liquid sample, see Figure 2.
FIG. 1: SEM images of the separator device fabricated in a single layer of Topas grade 5013 before sealing with a pyrex glass lid. The device height is 8.5 µm, the pillar diameter is 7 µm and the gap between neighboring pillars is 1 µm. The width of the inlet channels are 50 µm.

STAMP FABRICATION

The fabrication of our Topas based devices relies on NIL, where the stamp is made in silicon. Silicon is easily structured by standard cleanroom processing, i.e. UV lithography or electron beam lithography, deep reactive ion etching (DRIE) and thermal oxidation. The fabrication scheme for the stamps was presented earlier [13].

We have investigated two different kinds of anti-sticking layers (ASL) for the stamp. The first is a plasma deposited fluorocarbon film, consisting of C₄F₈ molecules adhering to the surface. Prior to coating, the stamps are etched in hydrofluoric acid (HF) for 10 s to remove any native oxide and impurities on the surface. The plasma deposition is performed in a DRIE tool (STS ICP Advanced Silicon Etcher), where the passivation step is modified to create an anti-sticking layer as suggested by Ayón et al. [12]. A 30 s long passivation step is used to create the fluorocarbon film on the stamp.

The second approach is vapor phase deposition (VPD) of long fluorocarbon chains, which are attached to a silane head group, in a self assembled monolayer [14, 15]. The molecules are deposited in a MVD-100 from Applied Microstructures [16]. Prior to coating, the stamp is treated in an oxygen plasma to remove any organic material on the surface, and to give a uniform surface hydroxylation. The chamber is evacuated and the perfluorodecytrichlorosilane precursor and catalyst vapor is injected into the chamber, where the silane head group reacts.
FIG. 2: The Lab-on-a-chip (LOC) device for absorbance measurements. A) SEM image of the imprinted microfluidic dye laser and Fresnel lens. B) Optical image of the absorption detection cell, planar waveguides and a focusing lens. C) Optical image of the LOC device.

with the hydroxyl groups on the silicon surface of the stamp by elimination of hydrochloric acid, thus binding covalently to the silicon surface. During this process the chamber is heated to avoid condensation of the vapors [17]. The advantage of using fluorocarbon chains attached to a silane head group is the strong adhesion between the silane head group and the stamp due to the creation of covalent bonds.
TABLE I: Measured contact angle ($\theta$) and surface roughness ($R_a$) of silicon stamps without any anti-sticking layer (ASL), stamps coated with fluorocarbon from a C$_4$F$_8$ plasma and stamps with vapor phase deposited ASL. The silicon and plasma deposited, C$_4$F$_8$, ASL are only imprinted into Topas grade 8007, whereas the vapor phase deposited ASL is imprinted into all three Topas grades.

Quality and durability of the anti-sticking layers were evaluated by means of surface energy, surface roughness, $R_a$, and durability tests by consecutive imprints in different Topas grades. The surface energy of the anti-sticking coating was evaluated by comparing the contact angle between the surface and water, see Table I. The measurements were made on a DSA 10 Mk 2 from Krüss. The contact angle for an uncoated silicon surface was found to be $73^\circ$. The contact angles for the plasma deposited, C$_4$F$_8$, and the VPD coating before use was found to be $110^\circ$ and $112^\circ$, respectively. The surface roughness, $R_a$, is measured by atomic force microscopy and found to be 0.0868 nm, 0.254 nm and 0.219 nm for a pure silicon surface, a plasma deposited, C$_4$F$_8$, and a VPD coating, respectively. The measurements are repeated after one imprint where the contact angles are $129^\circ$ and $114^\circ$, for the plasma deposited, C$_4$F$_8$, and the vapor phase deposited coatings, respectively. The surface roughness, $R_a$, is 2.11 nm and 0.173 nm for the plasma deposited, C$_4$F$_8$, and the vapor phase deposited coatings, respectively. The surface roughness, $R_a$, may significantly influence the contact angle of the plasma deposited, C$_4$F$_8$, coating, hence the contact angle is not a reliable measure for the surface energy. It was not possible to measure on the pure silicon stamp after one imprint due to sticking between stamp and polymer. After many consecutive imprints (so far 50 imprints without cleaning) the contact angle for the VPD coating is $108^\circ$ and the surface roughness is 0.616. However, this increase did not compromise the separation properties of stamps coated with a vapor phase deposited ASL. The plasma deposited, C$_4$F$_8$, coating withstands 2 to 3 imprints in Topas grade 8007, but no imprints in Topas grade 5013. These results are summarized in Table II.

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TABLE II: Comparison of the usability of different anti-sticking layers when imprinting a flat stamp into different Topas grades. A check mark indicates successful imprint and separation whereas a minus sign indicates unsuccessful separation.

<table>
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<th>SUBSTRATE PREPARATION</th>
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A thin film of Topas is spincoated onto the substrate. The Topas is supplied in solid pellet form, which must be dissolved in a non-polar solvent in order to obtain a usable resist solution for spin coating. The Topas is dissolved in Toluene in a closed container by ultrasonic agitation.

Prior to spin coating the substrates, silicon or silicon oxide, are cleaned in HF or 7-up (sulphuric acid and ammoniumperoxodisulphate at 80°C), respectively, to remove any native oxide or organic impurities from the surface. Subsequently the substrates are dehydrated on a hotplate at 150°C for 10 min. The dehydration ensures good adhesion between the Topas and the substrate. The substrates are spin coated with 3 ml of Topas solution in a manual spinner (Speedline Technologies P6204) at a suitable spin speed corresponding to the desired Topas thickness. Figure 3 shows spin curves for 29 wt.% Topas 5013, 23 wt.% Topas 8007 and 13 wt.% Topas 9506. The spin time is 60 s and after spinning the substrates are baked at 150°C for 10 min to remove the solvent. The surface roughness, $R_a$, of spin coated films of Topas grades, 9506, 8007 and 5013 are shown in Figure 4. The surface roughness of Topas grades 8007 and 5013, which are used to imprint the devices into is not critical, as long as the residual layer thickness is not important. However, the surface roughness of Topas grade 9506 used for the sealing of the devices is critical in order to get the structures into close contact with the lid, which is necessary to obtain an effective sealing. Thus, the Topas grade 9506 must be levelled before sealing. This is done by an imprint process using a flat VPD coated silicon stamp at a temperature of 145°C and a force of 15000 N on a 4-inch wafer. Cooling is initiated after 5 min and the force is released at a temperature of 60°C. Imprinting with a flat stamp reduces the surface roughness, $R_a$ by an order of magnitude, see Figure 4. The long range thickness of the Topas layer still varies across the wafer, but
FIG. 3: Spincurves for Topas grade 5013 29 wt.%, 8007 23 wt.% and 9506 13 wt.% in Toluene. The data points represent the average thickness across a 4-inch wafer and the error bars indicate the standard deviation on the data points. The dotted curves are simple power law fits of the data points.

The flexibility of the silicon and pyrex wafer is able to adapt for this.

IMPRINT

The imprinting is performed in an EVG 520HE nanoimprinter [18]. Table III shows the measured zero shear rate viscosities for Topas grade 9506, 8007 and 5013 respectively. The imprinting is performed at 200°C, well above the glass transition temperature for both Topas grade 8007 and 5013, see Table III, at an imprint force of 5000 N on a 4-inch wafer. The imprint force and temperature is kept for 10 min before cooling to 60°C where the imprint force is released and stamp and substrate are manually separated. To ensure a homogenous imprint two 0.5 mm thick graphite sheets are used on the chucks of the nanoimprint machine.

POST PROCESSING

Inlet and outlet holes are powder blasted through the substrate using aluminum oxide powder. A 10 µm thick layer of AZ4562 photoresist, baked at 50°C for 20 min, is protecting
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TABLE III: Glass transition temperature and zero shear rate viscosities for Topas grade 9506, 8007 and 5013, respectively. The viscosity was measured as a function of shear rate using a TA Instruments AR 2000 rheometer with 25 mm parallel plate geometry. The values for the zero shear rate viscosity was found by fitting a Carreau model to the data point.

The imprinted structures during the powder blasting. Furthermore, the front and backside of the wafer are covered with adhesive tape, which acts as a mask for the powder blasting. The adhesive tape is patterned by means of a CO₂ laser. After powder blasting, the adhesive tape is removed and the wafers are washed in DI-water for 5 min, and placed in an acetone bath for 4 min, to strip the photoresist followed by a 4 min rinse in DI-water.

The combined use of adhesive tape and a protective photoresist layer ensures that the imprinted structures are unharmed by the powder blasting process. It has been observed that cracks are induced in Topas grade 5013 when exposed to acetone, iso-propanol and photoresist. We speculate that the cracks are induced by environmental stress cracking [19] (ESC) which is a physical phenomenon that may occurs when a polymer is put under stress and exposed to a liquid environment. Such effects are not experienced for Topas grades 9506 and 8007. The stress is induced by the temperature cycle of the imprint process due to thermal mismatch between the silicon substrate (α_{Si} = 2.6·10^{-6} K^{-1}) and the Topas film (α_{Topas} = 0.6·10^{-4} K^{-1}). The results of ESC is an increase in surface roughness, Rₐ, as shown in Figure 4. By annealing at a designated temperature above Tₕ, the surface roughness can be decreased and the thermal history can be erased. However, a subsequent exposure to acetone, iso-propanol or photoresist will induce new cracks in the polymer film. For Topas based optical devices where control of the residual layer thickness is crucial, the residual layer may be removed by an oxygen plasma [9].

8
FIG. 4: Surface roughness of Topas grade 9506, 8007 and 5013 after spin coating, after levelling and after exposure to acetone 5 min measured between two scratches 500 µm apart. The error bars indicate the standard deviation.

SEALING

The imprinted structure is sealed with a pyrex glass lid, by means of an intermediate layer of polymer. Glass is often used for lids, as they allow visual inspection of the bonded structures as well as optical access to the microfluidic channels. Two kinds of polymers are used as intermediate layer, Topas grade 9506 and 950k poly-methylmethacrylate (PMMA). PMMA has previously been used as intermediate layer to seal microfluidic channels [7]. Prior to spin coating, the glass wafer is cleaned with X100 detergent and a 7-up etch (sulphuric acid and ammoniumperoxodisulfate at 80°C) for 10 min. Immediately before the spin process the wafer is baked at 150°C for 10 min to dehydrate the surface. 2.5 µm Topas or 2 µm PMMA is spun onto the glass wafer. The spin process is followed by a 10 min bake at 150°C on a hotplate.

The imprinted substrate and the glass lid are placed on top of each other, with the polymer layers face to face. This sandwich structure is pressed together in the imprinter at a force of 5000 N while the substrates are heated to a temperature between 70°C and 120°C. The force is applied when the substrates have reached the desired temperature. The bonding force is applied during cooldown and is not released before a designated temperature below the $T_g$ of the intermediate layer is reached.

Three different kinds of bonding sandwiches have been demonstrated. Topas grade 8007 to Topas grade 9506, and Topas grade 5013, to Topas grade 9506 and 950k PMMA, respec-
tively. The Topas grade 8007 to Topas grade 9506 bonding is made at 70°C and the Topas grade 5013 to Topas grade 9506 or 950k PMMA bonding is made at 120°C.

FABRICATED DEVICES

Two different devices have been fabricated: a particle separator and a LOC for absorption measurements.

The particle separator is a device separating particles in a liquid sample through deterministic lateral displacement, when operated in the laminar flow regime [11]. The active region of the device is a channel with an array of periodic obstacles, pillars in this design. Figure 1 shows a SEM picture of the device before sealing. The device height is 8.5 µm, the pillar diameter is 7 µm and the gap between neighboring pillars is 1 µm. The device has been fabricated in both Topas 8007 and 5013 and sealed with a Pyrex glass lid by an intermediate layer of Topas 9506 as described earlier. Besides inlet and outlet channels, the size of the active region is 3.2 mm×15 mm, which is imprinted perfectly with no defects when using stamps coated with VPD long fluorocarbon chains. The separation device has been tested with fluorescent latex beads with a mean diameter of 510 nm and a standard deviation of 5% [20]. The beads are dissolved in DI-water with 1 wt.% sodium dodecyl sulfate (SDS), which is necessary in order to wet the device because Topas is hydrophilic with contact angle 101°.

The contact angle of Topas can be reduced to less than 10° by a plasma treatment. Preliminary studies are being developed with a MW plasma (Iplas Cyranus I-6” Plasma System) in order to make the Topas more hydrophilic. Trials have been carried out in two different gas conditions: one with air and the other with a mixture of O₂ and Ar. Roughness remains unchanged after the plasma treatment. Contact angles less than 10° have been obtained with three different plasmas, listed in Table IV.

Figure 5 shows an image of the beads inside the device during operation. As seen, the beads are separated into two streams due to the size distribution of the beads. This verifies that the device separates beads larger than approximately 510 nm from beads with a diameter smaller than 510 nm.

The integration of an on-chip light source with optical elements, is demonstrated by integrating a microfluidic dye laser with an absorption detection cell by the use of fresnel
TABLE IV: Parameters for three different plasma treatments that reduces the contact angle of Topas to less than 10°.

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<td>O$_2$+Ar</td>
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<td>60</td>
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FIG. 5: Bead separation inside the pillar array of the separation device. Beads with an average diameter of 510 nm are separated into two streams (larger beads: top stream, smaller beads: bottom stream) due to the size distribution of the beads. The beads are dissolved in water with 1 wt.% SDS. The bright spots are beads sticking to the Topas surface.

lenses and planar waveguides, see figure 2. The device contains a microfluidic dye laser, which is based on high order Bragg reflection from an array of parallel microfluidic channels [13, 21], an absorption detection cell, fresnel lenses, planar waveguides and a microfluidic network. Fresnel lenses were chosen because they have less anti-guiding of the light due to their narrow design, when compared to conventional lenses. Furthermore they take up much less space on the chip than conventional lenses, thus allowing for a smaller device.

Solutions of Rhodamine 6G dissolved in ethanol or ethylene glycol are prepared, both
FIG. 6: Cracks (right) and no cracks (left) in Topas grade 8007. The cracks appear after long time exposure to a Rhodamine/ethanol solution. The cracks allows the dye solution access to the lens, thus destroying the functionality of the lens.

with a concentration of $2 \times 10^{-2}$ mol/L. The solutions are pumped through the chip with a flowrate of 50 µL/hr to avoid bleaching of the Rhodamine. The dye is optically pumped through the pyrex lid with a pulsed (10 Hz, 5 ns duration), frequency doubled Nd:YAG laser (Continuum Surelite I-10) emitting at 532 nm. The microfluidic dye laser emits light in the chip plane, which is focussed into the waveguide by the fresnel lens and guided to the edge of the chip, where it is collected by an optical fibre. The light is analyzed by a fixed grating spectrometer (AVS-USB2000 from Avantes). The laser is multimode and emits laser light at wavelengths between 576 and 590 nm. The lasing threshold is found to be 65 µJ/mm²

During operation it was observed that the Rhodamine/ethanol solution give rise to ESC in the polymer structures. These cracks allowed access for the solution to the fresnel lenses, thus destroying the functionality of the lens, see figure 6. Such effects were not observed for the Rhodamine/Ethylene glycol solutions.

CONCLUSION

NIL in Topas grades 8007 and 5013 have been investigated as a technology platform for fabrication of working lab-on-a-chip devices, including passive and active optical elements and microfluidics, demonstrating fabrication of millimeter to micrometer scale structures in a single fabrication step. We have shown that imprinting in Topas is challenging for the antisticking layer (ASL) of the stamp and only vapor phase deposition of long fluorocarbon chains is suitable as an antisticking agent for all grades of Topas. Furthermore, the vapor phase deposited ASL is far more durable compared to a plasma deposited, $C_4F_8$, fluorocar-
bon film. The surface roughness of spincoated Topas dissolved in Toluene is large making it difficult to make imprints with thin homogenous residual layers and makes levelling of the Topas surface necessary before sealing. Furthermore Topas grade 5013 is sensitive to environmental stress cracking (ESC). Thus, post processing on Topas 5013 is troublesome if ESC should be avoided.

Acknowledgement

The partial support of the EC-funded project NaPa (Contract no. NMP4-CT-2003-500120) is gratefully acknowledged. The contents of this work is the sole responsibility of the authors.

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