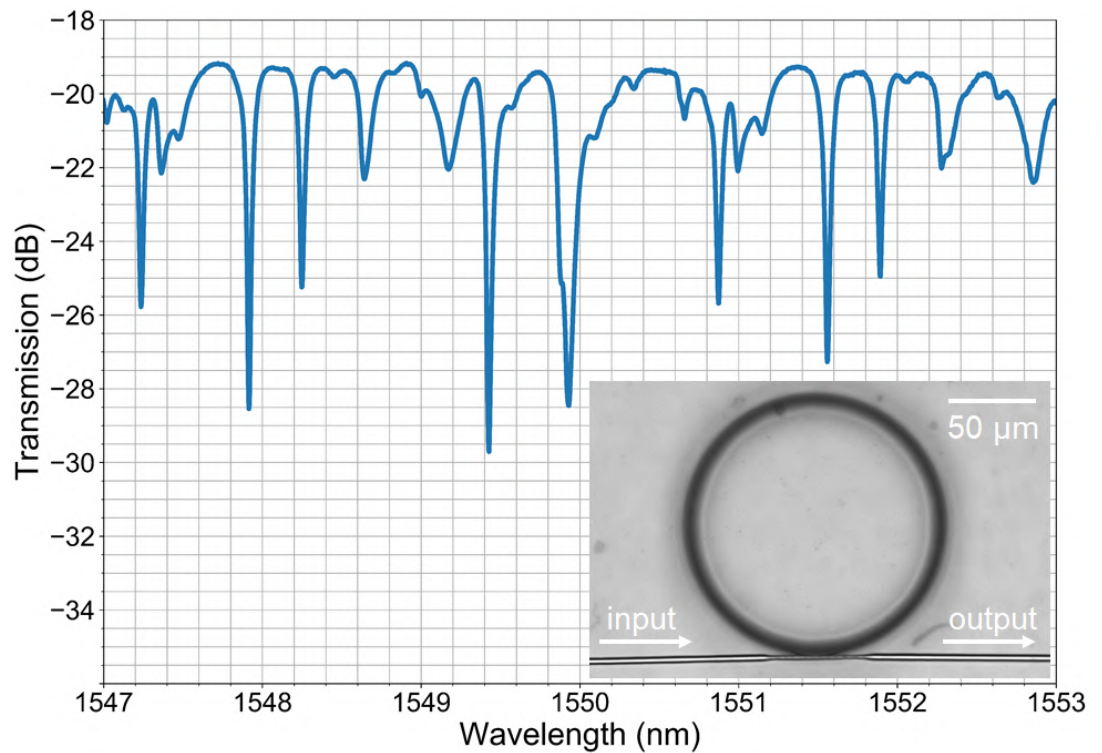




Fabrication of Optofluidic Systems by Femtosecond Laser Micromachining

João Miguel Mendes da Silva Maia

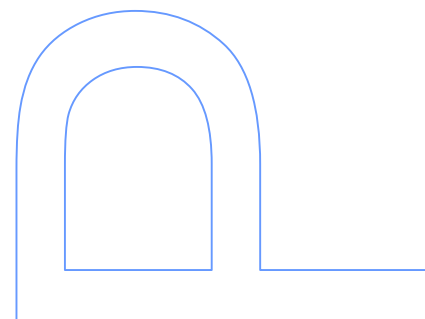
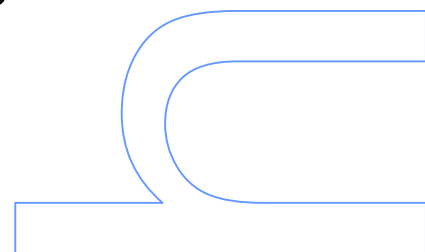
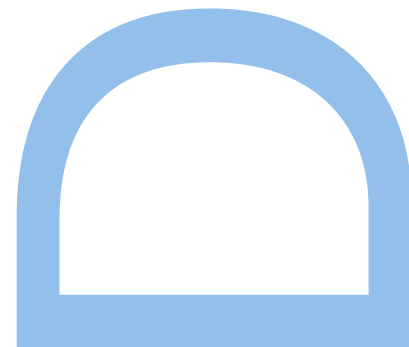
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Abstract

Since its inception, over more than two decades ago, ultrafast laser inscription has evolved into a versatile microfabrication technique capable of surface and volume processing of different classes of materials. Owing to their ultrashort pulse width and high peak intensity, the optical energy of a tightly focused laser beam can be delivered to the irradiated medium, in a controlled manner, via non-linear processes that induce a local modification of the structural properties of the exposed material. In fused silica, these may translate into an isotropic increase of the refractive index which enables the design of optical waveguides where light is guided through the modified path, or in the generation of etching selectivity that facilitates the formation of microfluidic channels due to the laser-modified volume being etched at a faster rate than the pristine medium. Further, due to the confined nature of the laser-induced modification, both structures can be combined in a single monolith along a user-defined three-dimensional architecture to form optofluidic devices.

Still, fused silica is a difficult material to machine which can restrict the potential of this technology. In particular, the formation of microstructures inside microfluidic channels is hampered due to the subtractive nature of the etching process. Additionally, chemical etching results in rugged machined surfaces that are incompatible with applications requiring a surface with optical-grade quality. These issues are addressed throughout this thesis, where the fabrication of optofluidic devices in planar fused silica substrates and oriented for label-free biosensing is also discussed in detail.

First, the fundamentals behind the laser-matter interaction are described, with special focus being given to the modifications induced in fused silica. To complement this review, the strengths and weaknesses of this technology are compared against those of conventional microfabrication techniques. The experimental procedures adopted during this work are then described together with the methods used to characterize the produced devices.

Afterwards, the fabrication of microfluidic channels is examined, being discussed the influence of the inscription and etching conditions on the etching selectivity and on the surface quality of their inner walls. An initial look into the integration of microfluidic channels with optical waveguides is made through the construction of Fabry-Pérot interferometers, where the channel serves a dual role as etalon and reservoir. The effects of the laser exposure parameters used to write the probing optical waveguide on the spectral quality of the measured signal are studied.

The fabrication of silica-based microstructures inside a microfluidic channel is then

addressed. The acquired control over the selective etching reaction enables the formation of micrometric-sized structures, whereas their surface roughness can be reduced to tens of nanometres by introducing a post-fabrication thermal annealing process. Suspended waveguides, consisting of a silica-core and a liquid-cladding, are fabricated and their waveguiding characteristics are analysed in detail. The fabrication of a monolithic whispering-gallery mode resonator, formed by a microdisk permanently coupled to a suspended waveguide responsible for the excitation of the optical modes of the resonator, is also discussed. The design of the device is carefully considered in order to tailor the geometry of the waveguide within the coupling region, and thermal-induced morphing is performed to place both microstructures tangent to each other. Whispering-gallery mode resonances can be excited with a high quality-factor. This work in particular conveys novel practical developments to the current state-of-the-art.

Keywords: chemical etching, glass machining, Fabry-Pérot interferometry, femtosecond laser direct writing, fused silica, integrated optics, optical sensing, optofluidics, whispering gallery mode resonator.

Resumo

Desde a sua primeira demonstração, há mais de duas décadas atrás, escrita com lasers pulsados de curta duração tornou-se numa técnica de microfabricação versátil capaz de produzir dispositivos em diferentes classes de materiais, tanto na sua superfície como no seu interior. Devido à duração ultracurta dos impulsos e às intensidades de pico elevadas, um feixe laser focado pode transferir a sua energia para o material irradiado de forma controlada e por processos não-lineares, que induzem uma modificação local das propriedades estruturais do material. Em sílica fundida, estas alterações podem conduzir a um aumento isotrópico do índice de refração que permite a construção de guias de onda ópticos onde a luz propaga-se através do caminho traçado pelo feixe laser, ou à geração de seletividade para fresagem química o que facilita a criação de canais de microfluídica dado que o volume modificado dissolve-se mais rapidamente do que sílica pura. Mais, dado que as modificações induzidas pelo feixe laser estão confinadas ao volume focal, estes dois tipos de dispositivos podem ser combinados numa geometria tri-dimensional e num único substrato para a realização de sistemas de optofluídica.

Contudo, sílica fundida é um material difícil de micromaquinar o que limita o potencial desta tecnologia. Em particular, a fabricação de microestruturas dentro de canais de microfluídica é dificultada pela natureza subtrativa do processo de fresagem química. Ainda, este processo resulta na maquinação de superfícies rugosas que são incompatíveis com aplicações onde é necessário uma superfície plana e de qualidade óptica. Esta tese procura resolver estes dois problemas, para além de também discutir em detalhe a fabricação de dispositivos de optofluídica para sensorização óptica em substratos planares de sílica fundida.

Em primeiro lugar, a interação entre radiação laser e o meio material e os respetivos processos subjacentes são descritos, sendo dado especial detalhe às modificações induzidas em sílica fundida. Para complementar esta introdução, os pontos fortes e fracos de micromaquinação com laser femtossegundo são ainda comparados contra os métodos de microfabricação convencionais. Os procedimentos experimentais utilizados neste trabalho são descritos em conjunto com as técnicas utilizadas para caraterizar os dispositivos fabricados.

De seguida, a fabricação de canais de microfluídica e a influência dos parâmetros de escrita e de fresagem química na seletividade no processo de fresagem e na rugosidade superficial das paredes dos canais é discutida. Uma primeira abordagem relativa à integração de canais de microfluídica com guias de onda ópticos é conseguida através da fabricação de interferómetros Fabry-Pérot, onde o canal de microfluídica serve dois

fins: cavidade Fabry-Pérot e reservatório para injeção e circulação do fluido em análise. A influência dos parâmetros de irradiação utilizados para a escrita do guia de onda, que sonda o interferómetro, nas propriedades espectrais do sinal medido é analisada.

A fabricação de microestruturas em sílica no interior de canais de microfluídica é depois discutida. O controlo adquirido sobre a reação de fresagem química seletiva permite a formação de estruturas com dimensão micrométrica, enquanto que a rugosidade superficial pode ser reduzida para dezenas de nanómetros após a realização de tratamento térmico. Guias suspensos, formados por um núcleo em sílica e por uma bainha líquida, são fabricados e é analisada em detalhe a guiagem de luz através dos mesmos. É ainda discutida a fabricação de uma cavidade óptica ressonadora numa geometria monolítica, formada por um microdisco acoplado permanentemente a um guia suspenso responsável pela excitação dos modos ópticos da cavidade. O dispositivo é desenhado por forma a permitir a maquinação com elevada precisão da geometria do guia suspenso na região de acoplamento, e o tratamento térmico é também realizado para permitir a colocação do guia suspenso tangente ao microdisco. A metodologia apresentada permite a excitação dos modos ressonantes da cavidade e com um fator de qualidade elevado. Este trabalho em particular expande o atual estado-da-arte.

Palavras-chave: cavidade óptica ressonadora, escrita direta com laser femtossegundo, fresagem química, interferometria Fabry-Pérot, maquinação de vidro, óptica integrada, optofluídica, sensorização óptica, sílica fundida.

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Nomenclature

2D	two-dimensional
2PP	two-photon polymerization
3D	three-dimensional
AFM	atomic force microscopy
APC	angled physical contact
ASE	amplified spontaneous emission
CAD	computer-aided design
CCD	charge-coupled device
DIC	differential interference contrast microscopy
FHD	flame hydrolysis deposition
fs	femtosecond
HF	hydrofluoric acid
KOH	potassium hydroxide
MDEA	methyl diethanolamine
MFD	mode field diameter
NA	numerical aperture
NBOHC	non-bridging oxygen hole centre
ODC	oxygen deficiency centre
OSA	optical spectrum analyser
PDMS	polydimethylsiloxane
PECVD	plasma-enhanced chemical vapour deposition
PEEK	polyether ether ketone

PETIA	pentaerythritol triacrylate
PM	polarization-maintaining
PMMA	polymethylmethacrylate
Q-factor	quality factor
RIU	refractive index unit
RMS	root-mean square
SEM	scanning electron microscopy
SiE'	silicon dangling bonds
SMF	single-mode fiber
SNR	signal-to-noise ratio
TE	transverse electric
TM	transverse magnetic
UV	ultraviolet
WGM	whispering-gallery mode

Chapter 1

Introduction

1.1 Motivation

At its core, ultrafast laser inscription is a material processing technique in which the energy from a tightly focused fs-laser beam is transferred into a transparent medium, due to non-linear absorption followed by relaxation and damage processes that locally alter the material properties. The first demonstration of this technique came in 1996 in a seminal paper by Hirao and co-workers [1], who demonstrated that fs-laser irradiation modified the optical properties of a small volume inside the bulk of glass substrates. Motivated by the unique features inherent to ultrafast laser inscription and aided by the parallel progress in laser technology, which made reliable turn-key fs-laser systems accessible to most laboratories, this microfabrication technique has gained increasing interest since then, as can be assessed from figure 1.1. Determinant to this growth were also the observations that this technique could be extended to different classes of materials, such as glasses [1], crystals [2], or polymers [3]. Further, the possibility for surface or volume machining with a spatial resolution of 0.1 to 1 μm while also facilitating the formation of unique three-dimensional architectures through selective laser patterning provided significant advantages over conventional lithography-based techniques. Moreover, due to being a direct and maskless technique, it enables rapid prototyping while avoiding the need for complex cleanroom facilities.

One of the first registered pathways for material transformation in glass media (e.g. fused silica, borosilicate glass) was linked to the isotropic increase of the refractive index within the focal volume. By scanning the sample across the focus of the laser beam, this property enabled the construction of optical waveguides where light is guided through the laser-modified path [1, 4]. As a result, initial interest of the technique was mainly directed to the fabrication of integrated optical devices.

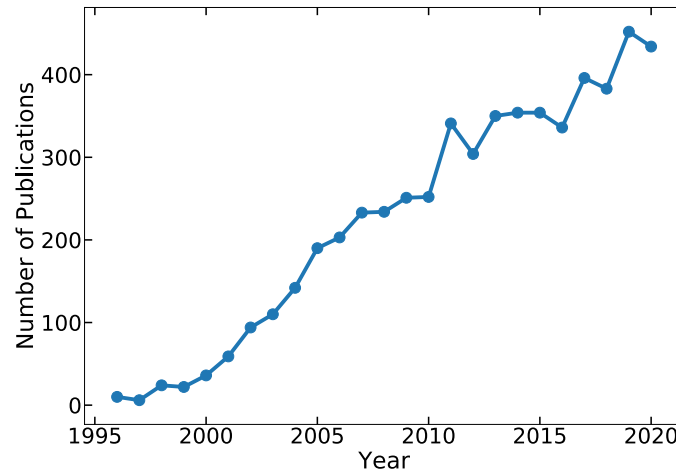


Figure 1.1: Number of publications related to fs-laser micromachining per year since 1996. Data obtained from the Scopus database.

Several authors have discussed the influence of the inscription parameters on the laser-induced refractive index contrast and on the guiding characteristics of the fs-laser written waveguides, and have demonstrated low-loss guiding in a broad wavelength range [5]. For instance, Fukuda *et al* [6] reported minimum propagation losses of 0.05 dB/cm at 1550 nm, comparable to the losses of devices made through planar lightwave circuit technology. Further, unlike in conventional techniques, the cross-sectional profile of fs-laser written waveguides can be effectively tailored through beam shaping methods [7, 8]. Making good use of the three-dimensional capabilities of this technique, S-bended waveguides with minimum radiation loss [6, 9] and multiplexers for coupling light into multicore fibers have also been reported [10]. Different configurations of 1-to-N power splitters, namely Y-junctions [11, 12, 13], directional couplers [14, 15] and multimode interference devices [16], or more complex geometries for channel multiplexing, such as add-drop filters [17] and arrayed-waveguide gratings [18], have also been discussed in detail. First-order Bragg grating waveguides were also shown by synchronously modulating the laser pulse train with the movement of the sample [19]. Phase-shift [20] and apodized gratings [21] were also demonstrated. Observation of this modification in doped-silica glasses and in crystals also enabled the production of active optical devices. For instance, Della Valle *et al* [22] reported an on-chip laser source in an Er-Yb-doped phosphate glass, where the fs-laser written waveguide provides a way for light to be guided along the substrate, whereas the optical gain from the host material is responsible for the light amplification. Meanwhile, fs-laser written waveguides in lithium niobate and in chalcogenide glasses also facilitated the realization of optical modulators [23, 24, 25] and non-linear photonic devices [26, 27, 28], respectively. Recently, three-dimensional waveguides written with ultrafast lasers have also found important applications in quantum circuits to replace the bulk optics in complex quantum optical systems [29, 30].

Meantime, another crucial advancement came in 2011 by Marcinkevicius *et al* [31] who reported the fabrication of microfluidic channels by noting that the laser-modified volume

was etched at a faster rate than pure fused silica, when immersing the sample in HF acid. Later on, it was shown that the generation of etching selectivity was linked to the formation of nanogratings, another possible laser-induced modification but almost exclusive to fused silica [32, 33]. Several authors have studied how the inscription parameters and etching conditions influence the formation of nanogratings, and how these can be optimized to maximize the etching selectivity and to form centimetre-long microfluidic channels with high aspect ratio [33, 34, 35, 36, 37, 38]. Further, by choosing an adequate patterning scheme, the size and shape of the cross-section of the microfluidic channel can be easily changed, contrary to what happens in conventional lithography-based techniques [39]. Moreover, it enables the production of three-dimensional microfluidic channels either at the surface or embedded in the fused silica substrate. Liu *et al* [40], for instance, formed a helical channel for rapid mixing of fluids via turbulent flow. Albeit through a different methodology, microfluidic channels can also be formed in other glasses through fs-laser micromachining [32, 41]. In Foturan glass, which is an amorphous material composed by a lithium aluminosilicate matrix doped with trace amounts of silver and cerium ions, an intermediate thermal annealing process is performed to crystallize the laser-modified volume, which is then etched in HF acid at a faster rate than the pristine medium [42]. Microfluidic channels can also be formed through water-assisted laser ablation, which, unlike the previous two methods, is a subtractive process that does not require generation of etching selectivity [43]. Instead, the high energy of the incident fs-laser pulses causes micro-explosions that eject the material from the focal volume, while water circulating inside the microfluidic channel removes the debris. As it relies on laser ablation, this technique can be applied to a wider range of glasses. For instance, it is used to fabricate microfluidic channels in borosilicate glass [44, 45], where the formation of nanogratings is not observed [32]. However, the length of the microfluidic channel is limited to around 100 μm to 1000 μm due to accumulation of debris and eventual clogging, which is caused by the inability of water to efficiently remove the ejected material as the length of the channel increases. Porous glasses, meanwhile, can be used to solve this issue as the water supply is guaranteed due to capillarity [46].

Due to the confined nature of the laser-induced modification, the integration of optical circuits with microfluidic systems in a glass substrate is also more straightforward through fs-laser micromachining than through photolithography or soft lithography techniques. This advantage has also been essential in the development of optofluidic devices, a research field that exploits the combination of both systems and further extends the applications of this microfabrication technique into the domains of biology and analytical chemistry. In particular, the realization of lab-on-a-chip biological platforms, which enable testing of chemical reactions with nanolitre volumes and provides enhanced sensitivity, is made possible by fs-laser micromachining.

Several examples of such devices can be found in the literature. For instance, Hwang *et al* [47] fabricated a real-time red blood cell counter in a fused silica chip formed by a microfluidic channel orthogonally crossed by a fs-laser written waveguide, which detected the presence of cells through the measurement of intensity variations caused

by the passage of a cell through the intersection region. The same research group also reported on a similar device, where the presence of red blood cells was instead assessed by measuring its fluorescence induced by light propagating through the fs-laser written waveguide [48]. Through a similar configuration illustrated in figure 1.2(a), optical trapping of red blood cells flowing through a microfluidic channel induced by light guided through a fs-laser written waveguide was also demonstrated [49, 50]. Based on the emitted fluorescence or on the light-induced deformation properties of optical-trapped cells, cell sorting devices were also constructed on fused silica chips [51, 52]. Alternatively, optical sensors based on label-free detection have also been reported. For instance, figure 1.2(b) shows a Mach-Zehnder interferometer, fabricated by Crespi *et al* [53], entirely made in a fused silica chip for refractive index sensing, where the sensing arm is composed by an optical waveguide that orthogonally crosses a microfluidic channel while the reference arm corresponds to a waveguide that goes under the channel. Refractive index sensors composed by a Bragg grating waveguide formed near a microfluidic channel, such that the reflected wavelength is influenced by the refractive index of the fluid inside the channel, were also reported [54, 55]. Fs-laser irradiation can also assist in other processes, such as in the deposition of metallic layers at the surface of the microfluidic channel, to provide enhanced functionalities. For instance, Xu *et al* [56] developed a surface-enhanced Raman spectroscopy micromonitor for the detection of biomolecules, where fs-laser irradiation was employed to photoreduce silver particles, initially present on a silver nitrate solution injected inside a microfluidic channel made at the surface of a glass substrate, which then deposited at the surface of the channel.

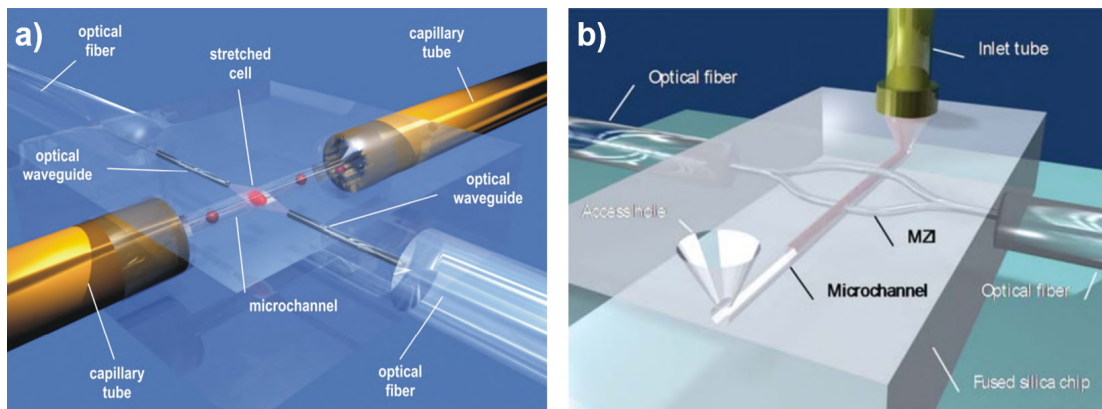


Figure 1.2: Schematic of (a) a monolithic chip for optical trapping and stretching of single cells and of (b) an integrated Mach-Zehnder interferometer for optical sensing. Image (a) was taken from [49], and image (b) from [53].

Further, owing to the selective etching reaction, microstructures can also be produced inside microfluidic channels for enhanced functionalities by carefully patterning the fs-laser beam irradiation path. For example, figure 1.3(a-b) shows a microcube and a microsphere formed inside a microfluidic channel through selective etching [57]. Micro-optical mirrors and lenses have also been fabricated directly in glass through this approach [58, 59]. Moreover, Lin *et al* [60] and Song *et al* [61] formed microtoroids supported by a thin pedestal inside a microfluidic channel made at the surface of a

fused silica substrate, as illustrated in figure 1.3(c). By following the fabrication with post-processing thermal treatment, they were able to excite whispering-gallery mode resonances through the evanescent coupling of a free-standing tapered fiber and through welding via CO₂ laser irradiation of a tapered fiber to the microresonator, respectively. In a Corning EAGLE XG glass substrate, Spagnolo *et al* [45] also demonstrated optical modulation and switching based on an oscillating $40 \times 240 \times 1000 \mu\text{m}^3$ cantilever fabricated inside a microfluidic channel through water-assisted laser ablation. As depicted in figure 1.3(d), light guided through a fs-laser written optical waveguide written within the cantilever periodically coupled light into one or more optical waveguides that continued throughout the substrate beyond the cantilever's tip, with a modulation period dependent on the amplitude and frequency of the mechanical oscillation. Similarly, Ceccarelli *et al* [44] constructed a reconfigurable Mach-Zehnder interferometer in a Corning EAGLE XG chip for optical phase shifting, where the pristine material surrounding the sensing arm was removed through water-assisted laser ablation. A phase shift between both arms could be induced by dissipating electrical power with a microheater placed above the sensing arm, where the minimum power to induce a 2π phase shift and thermal cross-talk were reduced due to the sensing arm being isolated.

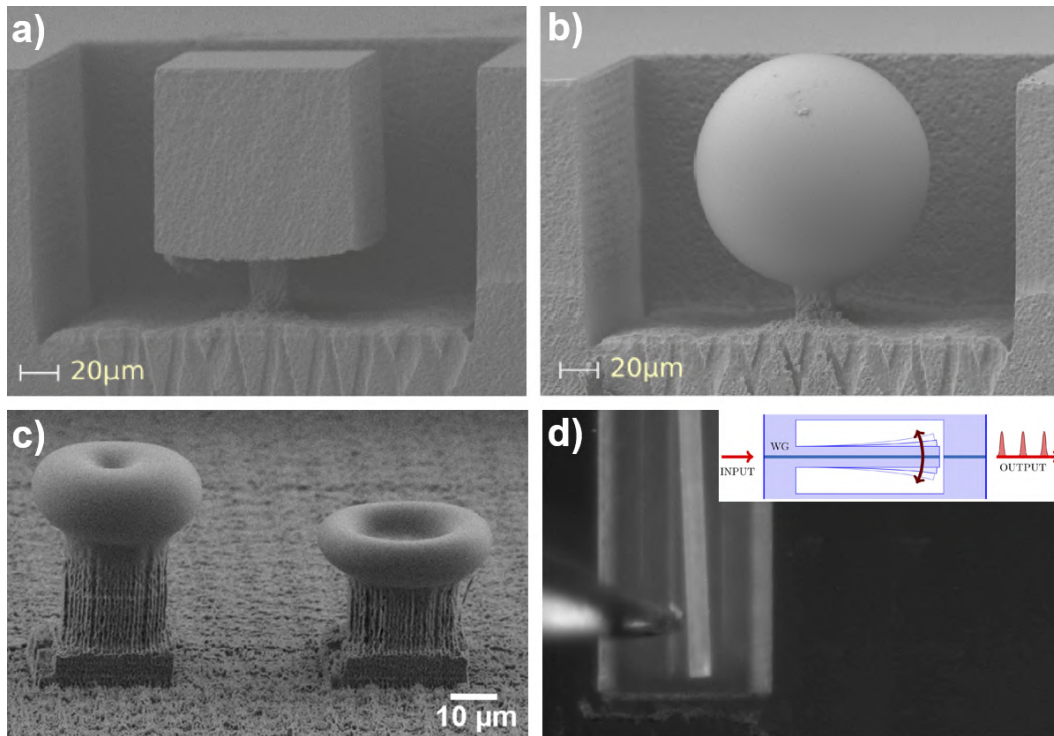


Figure 1.3: SEM images of (a-b) a silica-based microcube supported by a thin pedestal that morphed into a microsphere through laser-induced morphing, and of (c) silica-based microtoroidal cavities obtained through fs-laser irradiation followed by chemical etching and CO₂ laser polishing for excitation of WGMs. (d) Optical microscope image of a slightly deflected glass cantilever made inside a microfluidic channel for optical modulation. The inset shows the conceptual scheme of the device. Images (a-b) were taken from [57], image (c) from [60], image (d) from [45].

On the other hand, additive techniques such as multiphoton polymerization

triggered by fs-laser irradiation can also be used for the same end [3, 62]. In particular, the inherent high spatial resolution of 100 to 200 nm, well beneath the Rayleigh criterion, in combination with stage movement can be used to form micrometric-sized three-dimensional structures. Enhanced fluid handling capabilities have been demonstrated in microfluidic channels made at the surface of glass substrates, through the fabrication of filters consisting of a porous sheet containing openings of variable size and shape [63, 64] and through the fabrication of micromixers comprising multiple polymeric layers that turned the flow chaotic and improved the mixing efficiency [65], as illustrated in figure 1.4 (a) and (b) respectively. The direct interaction between polymeric micro-optical elements with the fluid present in the microfluidic channel can also be used in optical sensing applications. With an optical waveguide crossing a microfluidic channel containing a polymeric inverted-woodpile structure that operated as a photonic crystal, Haque *et al* [66] realized a refractive index sensor by measuring the shift in the photonic bandgap location caused by the variation in the refractive index of the surrounding fluid. Kelemen *et al* [67] also fabricated a polymeric microring inside a microfluidic channel for refractive index sensing, whose WGM resonances were excited by a suspended waveguide anchored to both walls of the microfluidic channel and attached to the microring; the resonant wavelength of the excited modes depended on the refractive index of the surrounding fluid.

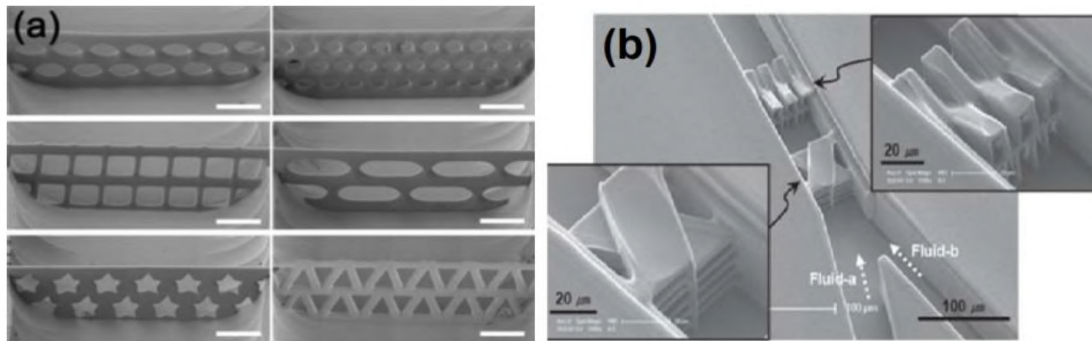


Figure 1.4: SEM images of (a) microsieves with openings of different sizes and shapes for particle filtering and (b) a crossing manifold micromixer embedded in a Y-branched microfluidic channel. Image (a) was taken from [63], and image (b) from [65].

Still, some issues, which extend from more fundamental questions related to the laser-matter interaction itself to more practical challenges, hinder the potential and mass application of this technique [68]. In particular, ultrafast laser inscription is a serial processing technique which translates into a lack of scalability and into a low throughput. Aided by the development of novel ultrafast laser systems, several researchers have looked into decreasing the fabrication time by writing at higher scanning speeds, close to a meter-per-second, while proportionately increasing the laser repetition rate [69, 70], and by using galvanometric mirrors combined with linear stage movement [71]. Different beam shaping techniques, for instance programmable beam splitting and on-axis multipoint focusing, have also been tested to allow parallel processing [72].

Further, microfluidic channels formed through fs-laser micromachining possess a

surface roughness around 100 nm and are characterized by a long-range modulation related to the laser writing pattern [73]. In the context of optofluidics, rugged surfaces create significant loss and distort the beam wavefront, turning these systems incompatible for applications requiring an optical-grade surface quality [68]. In addition, although some articles have pointed to the fabrication of microstructures inside microfluidic channels, the subtractive nature of etching or water-assisted ablation processes leads to a poor resolution which ranges from a few to tens of micrometers [74]. Although multi-photon polymerization could be used to circumvent this problem, as it enables the formation of smooth and uniform three-dimensional polymeric structures with sub-100 nm feature size, the use of polymers comes at a loss. In comparison with glasses, polymers generally exhibit higher optical losses than glasses, with fused silica still being the industry standard material in optical communications. Polymeric structures are also known to be more fragile and can be dissolved more easily in solvents, whereas fused silica shows long term stability and is a biocompatible material. In this sense, the fabrication of glass-microstructures through fs-laser irradiation followed by chemical etching is more appealing.

Therefore, the goal of this thesis is to fabricate optofluidic devices in fused silica planar substrates through fs-laser micromachining while addressing these limiting issues. Two configurations, namely a Fabry-Pérot interferometer and a whispering-gallery mode resonator, are constructed and tested as refractometers. The fabrication of microfluidic channels is carefully analysed, with the influence of the writing and etching parameters on the etching selectivity and quality of the channel surface being considered in detail. Novel design schemes are adopted, which, together with the high control acquired over the selective etching process, enable the formation of three-dimensional silica-made microstructures inside a microfluidic channel. Microstructures with minimum dimension of 2 μm can be machined, whereas post-fabrication thermal annealing is routinely added to smoothen the microstructures' surface to an average roughness of 10 nm and, in some cases, to also morph the machined structure into a circular shape.

1.2 Organization of the Thesis

The thesis is organized in six chapters. **Chapter 1** provides an overview of the context of this thesis and a general review of the current state-of-the-art, from which the motivation and objectives for this work are defined. The main publications that resulted from this thesis are enumerated as well.

Chapter 2 describes the basic theory behind the interaction between ultrashort laser pulses and transparent media. The induced modifications upon irradiation of fused silica are highlighted, with special insight being given to the material transformations linked to an isotropic increase of the refractive index and to the formation of nanogratings. The composition and morphology of the laser-modified volume is also examined, alongside the respective formation models.

Chapter 3 is dedicated to the methods and tools used in this research process to

fabricate and characterize the proposed optofluidic devices.

Chapter 4 focuses on the fabrication of microfluidic channels at the surface of fused silica planar substrates. The influence of the inscription and etching parameters on the properties of the microfluidic channel are assessed, as well.

Chapter 5 discusses the fabrication of a Fabry-Pérot interferometer. Some considerations regarding the design of the microfluidic channel, which operates as etalon, are made in order to minimize surface imperfections. The effect of the inscription parameters used to write the probing waveguide on the spectral quality of the measured signal is also determined. After this calibration, operation of the device as a refractometer and as a magnetic field sensor is shown.

Chapter 6 is dedicated to the construction of a monolithic whispering-gallery mode resonator inside a microfluidic channel. Targeted patterning with the fs-laser beam enables the production of microstructures inside a microfluidic channel due to the selective etching mechanism, while thermal annealing is performed to decrease their surface roughness. The design and fabrication of suspended waveguides and microdisk resonators is first examined separately. In particular, the guiding characteristics and optical losses of solid-core liquid-cladding waveguides is experimentally studied and compared to the results predicted by waveguiding theory. Then, several design and fabrication methods for the integration of both microstructures are proposed and tested. Thermal-induced morphing, in particular, is shown to enable optical coupling between both, and therefore to allow the excitation of whispering-gallery modes of the microresonator. Operation of the resulting device as a refractive index sensor is also demonstrated. The fabrication of polymeric suspended waveguides inside a microfluidic channel through self-guiding polymerization is also briefly discussed in **annex B**.

Lastly, **chapter 7** includes a brief summary of the main findings of this work and some suggestions for future work.

1.3 List of Publications

The research work detailed in this thesis led to the publication of two articles in peer-reviewed international journals and of a book chapter, and to six communications in conferences (five in international ones, and two in national ones). Together with the work developed by other colleagues of the research group, three invited talks in international conferences were also given.

Besides, the cooperation with other colleagues through assistance in the fabrication procedure and/or in the analysis and discussion of the experimental results led to the co-authority of eight publications in international journals and of fifteen communications in international and national conferences.

This set of publications and communications is listed below.

Publications in Peer-Reviewed International Journals

João M. Maia, Vítor A. Amorim, Duarte Viveiros and P. V. S. Marques, Femtosecond Laser Micromachining of an Optofluidics-based Monolithic Whispering-Gallery Mode Resonator Coupled to a Suspended Waveguide, *Nature Scientific Reports* 11, art. no. 9128, 2021. DOI: 10.1038/s41598-021-88682-x

Duarte Viveiros, José M. M. M. de Almeida, Luís Coelho, Helena Vasconcelos, Vítor A. Amorim, **João M. Maia**, Pedro A. S. Jorge and Paulo V. S. Marques, Turn Around Point Long Period Fiber Gratings fabricated by Femtosecond Laser Direct Writing and Coated with Titanium Dioxide, *Journal of Lightwave Technology* 39(14), 2020. DOI: 10.1109/JLT.2021.3078257

Vítor A. Amorim, Duarte Viveiros, **João M. Maia** and P. V. S. Marques, Intensity-modulated refractometer based on mode-mismatch in surface waveguides inscribed by femtosecond laser direct writing, *Optics & Laser Technology* 135, art. no. 106723, 2021. DOI: 10.1016/j.optlastec.2020.106723

Vítor A. Amorim, **João M. Maia**, Duarte Viveiros and P. V. S. Marques, Mach-Zehnder Interferometer-Based Evanescent Refractometer Inscribed at the Surface of Eagle 2000 by Femtosecond Laser Writing, *IEEE Sensors Journal* 21(2), 1603-1608, 2020. DOI: 10.1109/JSEN.2020.3021586

Duarte Viveiros, Vítor A. Amorim, **João M. Maia**, Susana Silva, Orlando Frazão, Pedro A. S. Jorge, Luís A. Fernandes and Paulo V. S. Marques, Femtosecond laser direct written off-axis fiber Bragg gratings for sensing applications, *Optics & Laser Technology* 128, art. no. 106227, 2020. DOI: 10.1016/j.optlastec.2020.106227

Vítor A. Amorim, **João M. Maia**, Duarte Viveiros and P. V. S. Marques, Inscription of surface waveguides in glass by femtosecond laser writing for enhanced evanescent wave overlap, *Journal of Optics* 22(8), 2020. DOI: 10.1088/2040-8986/aba03f

Duarte Viveiros, José M. M. M. de Almeida, Luís Coelho, Helena Vasconcelos, **João M. Maia**, Vítor A. Amorim, Pedro A. S. Jorge and Paulo V. S. Marques, Temperature Stability and Spectral Tuning of Long Period Fiber Gratings Fabricated by Femtosecond Laser Direct Writing, *Sensors* 20(14), 2020. DOI: 10.3390/s20143898

João M. Maia, Vítor A. Amorim, Duarte Viveiros and P. V. S. Marques, Magnetic field sensors in fused silica fabricated by femtosecond laser micromachining, *Journal of Physics: Photonics* 2(1), 2019. DOI: 10.1088/2515-7647/ab6711

Vítor A. Amorim, **João M. Maia**, Duarte Viveiros and P. V. S. Marques, Loss Mechanisms of Optical Waveguides Inscribed in Fused Silica by Femtosecond Laser Direct Writing, *Journal of Lightwave Technology* 37(10), 2240-2245, 2019. DOI: 10.1109/JLT.2019.2900913

Vítor A. Amorim, Duarte Viveiros, **João M. Maia** and P. V. S. Marques, Mass Produccible Low-Loss Broadband Optical Waveguides in Eagle2000 by Femtosecond Laser Writing, *IEEE Photonics Technology Letters* 31(20), 1658-1661, 2019. DOI: 10.1109/LPT.2019.2942104

Book Chapter

João M. Maia, Vítor A. Amorim, D. Alexandre and P. V. S. Marques, Advances in Fs-Laser Micromachining Towards the Development of Optofluidic Devices, in Optics, Photonics and Laser Technology 2017 (pages 119-144), Springer Series in Optical Sciences, May 2019. DOI: 10.1007/978-3-030-12692-6

Invited Talks in International Conferences

Paulo V. Marques, Vítor A. Amorim, **João M. Maia** and Duarte Viveiros, Loss Mechanisms in femtosecond laser written optical waveguides, SPIE Photonics West, Frontiers in Ultrafast Optics: Biomedical, Scientific, and Industrial Applications XXI, 6-11 March 2021.

Paulo V. S. Marques, **João M. Maia**, Vítor A. Amorim and Duarte Viveiros, Femtosecond Laser Fabrication of Monolithic Low Loss High Quality Optical Waveguides and Microfluidic Channels for Optical Sensing Applications, PIERS 2019, Rome, Italy, 17-20 June 2019.

P.V.S. Marques, Vítor A. Amorim, **João M. Maia**, D. Alexandre and Duarte Viveiros, Fabrication of Monolithic Add-Drop Filters in Pure Silica by Femtosecond Laser Writing, ICTON 2018 - 20th International Conference on Transparent Optical Networks, Bucharest, Romania, 2018. DOI: 10.1109/ICTON.2018.8473735

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João M. Maia, Vítor A. Amorim, Duarte Viveiros and P. V. S. Marques, Fs-Laser Micromachining of a Monolithic Whispering Gallery Mode Resonator Coupled to a Suspended Waveguide, accepted to the EOS Annual Meeting (EOSAM) 2021 to take place in 13-17 September 2021 in Rome, Italy

Duarte Viveiros, José M. M. de Almeida, Luís Coelho, Helena Vasconcelos, **João M. Maia**, Vítor A. Amorim, Pedro A. S. Jorge and Paulo V. S. Marques, Femtosecond Laser Direct Writing of Turn Around Point Long Period Fiber Gratings Coated with Titanium Dioxide for Improved Sensitivity, accepted to the 27th International Conference on Optical Fibre Sensors 2020.

Duarte Viveiros, José M. M. de Almeida, Luís Coelho, Helena Vasconcelos, Vítor A. Amorim, **João M. Maia**, Pedro A. S. Jorge and Paulo V. S. Marques, Femtosecond laser written long period fibre gratings coated with titanium dioxide for improved sensitivity, Optical Sensing and Detection VI, 113540C, 1 April 2020. DOI: 10.1117/12.2555686

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Hugo J. da Nóbrega, Vítor A. Amorim, **João M. Maia**, Paulo V. S. Marques, Manuel A. Alves and Francisco J. Galindo-Rosales, OpenFOAM® and μ PIV-aided femtosecond

irradiation-based etching optimization for applications in microfluidics, IBEREO 2019, Porto, Portugal, 4-6 September 2019.

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Vítor A. Amorim, **João M. Maia**, Duarte Viveiros and P. V. S. Marques, Addressing the Fabrication Difficulties of Femtosecond Laser Written Surface Waveguides for Enhanced Evanescent Coupling, 5th Conference on Optofluidics, EOS Optical Technologies, Munich, Germany, 24-26 June 2019. DOI: 10.1051/epjconf/201921515003

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Duarte Viveiros, **João Maia**, Vítor A. Amorim, Pedro A. S. Jorge and P. V. S. Marques, Fabrication of periodic structures in optical fibers by femtosecond laser micromachining for sensing applications, IV International Conference on Applications of Optics and Photonics, Lisbon, Portugal, 31 May - 4 June 2019. DOI: 10.1117/12.2527261

Vítor A. Amorim, **João M. Maia**, Duarte Viveiros and P. V. S. Marques, Optical and microfluidic monolithic devices fabricated by femtosecond laser micromachining, Optics 2018 – 6th International Symposium in Optics and its Applications, Trento, Italy 2018.

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João M. Maia, Vítor A. Amorim, Duarte Viveiros and P. V. S. Marques, Femtosecond laser micromachining of Fabry-Pérot interferometers in fused silica for refractive index sensing, Proc. SPIE 11207, Fourth International Conference on Applications of Optics and Photonics, 1120712, in IV International Conference on Applications of Optics and Photonics, Lisbon, Portugal, 31 May - 4 June 2019. DOI: 10.1117/12.2527302

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Oral Communications in National Conferences

João M. Maia, Vítor A. Amorim, Duarte Viveiros and P. V. S. Marques, Fabry-Pérot Interferometer fabricated in fused silica through femtosecond laser micromachining, Symposium on Engineering Physics, 3rd Doctoral Congress in Engineering, Porto, Portugal, 27-28 June 2019.

Vítor A. Amorim, **João M. Maia**, D. Viveiros and P. V. S. Marques, Low-loss broadband femtosecond laser written surface waveguides for enhanced evanescent coupling, Symposium on Engineering Physics, 3rd Doctoral Congress in Engineering, Porto, Portugal, 27-28 June 2019

Duarte Viveiros, **João M. Maia**, Vítor A. Amorim, Pedro A. S. Jorge and P. V. S. Marques, Fabrication of periodic structures in optical fibers by femtosecond laser micromachining, Symposium on Engineering Physics, 3rd Doctoral Congress in Engineering, Porto, Portugal, 27-28 June 2019.

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Chapter 2

Fundamentals of Femtosecond Laser Micromachining

This chapter starts by reviewing and by discussing the strengths and weaknesses of traditional techniques adopted in the fabrication of integrated optical devices and microfluidic systems. This is followed by a general description of the interaction between a fs-laser beam and a transparent medium, which, in short, comprises non-linear absorption and ionization, ensued by electronic relaxation and deposition of laser energy within the lattice with consequent material modification; this section is completed by considering the propagation of fs-laser pulses along the irradiated medium. With fused silica as the adopted material throughout this dissertation, a detailed analysis of the main laser-induced modifications observed in this glass is provided. Special attention is dedicated to the material transformations associated with an isotropic increase of the refractive index and with the formation of nanogratings, as these are the main modifications underlying the fabrication of the optofluidic devices reported in this thesis. Their morphology and composition are discussed, alongside the prevalent formation models.

2.1 Traditional Fabrication Techniques

The maturity of photolithography and etching-based technologies, which evolved from the microelectronic and semiconductor industries, was one of the major reasons behind the use of these processes in integrated optics and microfluidics. In spite of still being the industry standard for most applications, these techniques present some limitations regarding the fabrication of optofluidic devices. In particular, integration of optical and microfluidic systems and fabrication of three-dimensional microstructures has proven to be a challenging and cumbersome process. Here, due to their significance and to better comprehend the advantages and disadvantages of fs-laser micromachining, these techniques are reviewed.

2.1.1 Microfluidic Systems

Historically, microfluidic systems were first produced by combining photolithography and etching techniques [75]. Photolithography is a multistep technique involving transfer of a designed pattern from a mask onto a surface, and whose fabrication procedure is illustrated in figure 2.1. In short, a clean and dehydrated silicon or glass substrate is spin-coated with a positive or negative tone photoresist. To enhance its adhesion to the substrate, an adhesion promoter coating can be done prior to this step. After soft baking at around 80-110°C, which is done to further improve the adhesion of the photoresist to the substrate by solvent evaporation and built-in stress removal, the structure is exposed to a radiation source through a photomask. Conventionally, it is used a chrome mask, which is more resistant and stable and provides a better resolution, that is obtained by sputtering a chrome layer onto a glass substrate in which the designed pattern is etched. The mask can be also designed in a CAD file and printed onto a high-resolution transparency which, nevertheless, offers poor spatial resolution that translates into a lack of definition of the boundaries and increased wall roughness. The exposure is usually done in contact method where the mask is held against the photoresist, thereby leading to a 1:1 replication. One of the issues during this step is that the resolution is limited by the Rayleigh diffraction criterion; in conventional lithography the minimum feature size obtained is of the order of 1 μm . A better resolution, around 10 nm, can be achieved through deep UV exposure or electron-beam lithography at the expense of a longer exposure time. After this step, post-exposure baking may be necessary to promote photoresist adhesion and to increase its resistance to etching. Then, the substrate is rinsed in a developing solution where the unwanted and soluble photoresist is removed, leaving the exposed/unexposed pattern on the substrate's surface (depends if the photoresist is positive/negative, respectively). Lastly, a hard bake step is conducted to strengthen the photoresist.

The photolithography procedure is succeeded by an etching process, where the photoresist layers protect the underlying material from being removed. Both wet etching (material is removed by liquid chemicals) or dry etching (plasmas or etchant gases remove the material through a physical and/or chemical reaction) processes may be performed depending on the desired feature depth and aspect ratio. Generally, though, reactive ion etching is used. Afterwards, the remaining photoresist is removed, leaving behind an open channel at the surface of the substrate. Note that, in some cases, the photoresist itself is not enough as a mask for dry-etching. On that situation, a metallic layer is deposited prior to the photoresist, and the resist layer is used to define the pattern on the metallic layer. After metal wet-etching, the photoresist is dissolved leaving behind a metallic mask ready for etching.

A variety of techniques can be used to seal the device by bonding the open surface to glass or silicon substrates [76]. In anodic bonding, application of an electric field promotes ion migration and oxidation, thereby changing the surface chemistry and forming a bond between both substrates. In thermal fusion bonding, the substrates are heated to a temperature slightly above the material's transition temperature while applying

pressure to increase contact forces; after cooling, both substrates become permanently bonded. One major issue is channel deformation caused by unoptimized temperature and/or pressure or due to different thermal expansion coefficients from the materials that compose the substrates to be sealed. Both anodic and thermal bonding also require high pressures, voltages and/or temperatures that can damage or even break the entire structure. Adhesive bonding relaxes some of these requirements. In this indirect bonding technique, an adhesive layer (epoxy or photosensitive glue) is placed between the two substrates and adheres to them due to evaporation of the solvent or due to polymerization induced by UV irradiation, respectively. The main challenge is in obtaining a uniform thickness along large surfaces and avoiding clogging of microfluidic channels during bonding. After sealing, openings for fluidic interconnection are usually made in the cover layer either by deep reactive ion etching, by drilling or by laser ablation.

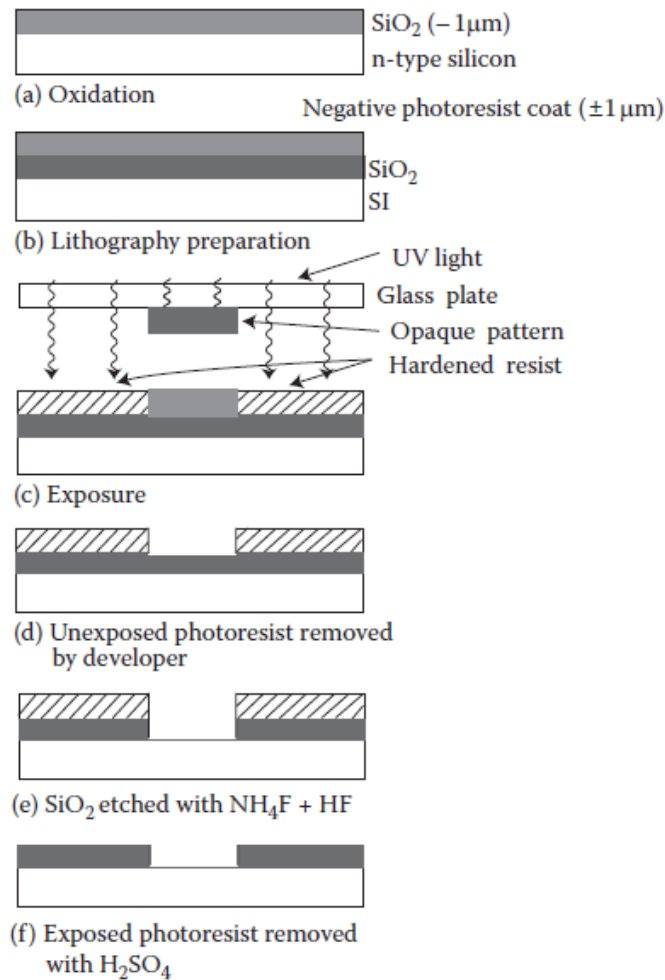


Figure 2.1: Photolithography with a negative-tone photoresist. Image was taken from [75].

Despite still being extensively employed, photolithography is nonetheless a planar technique which means that 3D structures are fabricated through stacking of multiple 2D structures, making the entire process time-consuming and complex. Further, this technique requires access to specialized cleanroom facilities, in order to control and minimize the level of contaminants (dust, microorganisms, chemical vapours) that are

incorporated in the device.

The high cost of photolithography has also led to the development of cheaper fabrication techniques based on the replication of a master template (micromolding) [77]. The master structure consists of a relief pattern generally produced through photolithography and etching, which can be replicated many times before starting to degrade. Generally, there is a 1:1 correspondence between the dimensions of the features of the master structure and those of the final device. Micromolding can occur through three main techniques: soft lithography (most common), hot embossing and injection molding, all of which are depicted in figure 2.2. Devices with features as small as tens of nanometres can be produced, with the resolution of each technique being mainly limited by the resolution with which the master template is produced.

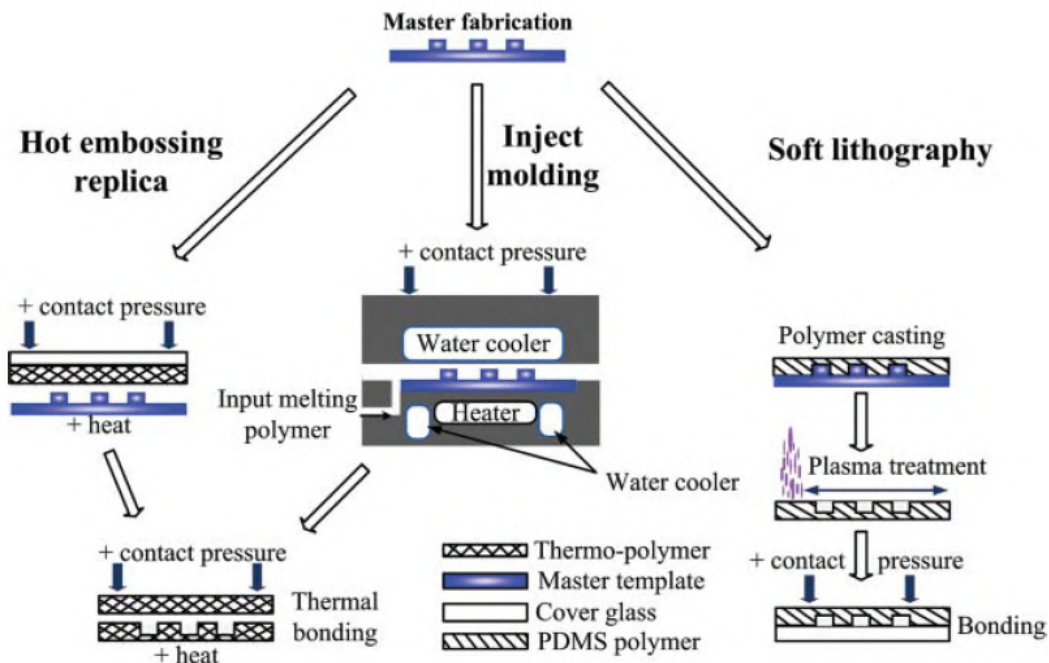


Figure 2.2: Micromolding techniques. Image was taken from [77].

Soft lithography is a rather straightforward replication technique mainly used for the production of microfluidic devices in PDMS, which is an optically transparent and durable elastomeric polymer [78]. The fabrication procedure is less dependent on environmental conditions and can be carried out in a normal laboratory. PDMS is usually supplied in two components, a base and a curing agent. Both agents are mixed typically in a 10:1 ratio (base:curing agent mass), however this ratio can be varied to provide better sealing or to change the polymer's mechanical properties (after curing). The solution is then stirred and degassed to remove the air bubbles that appear during mixing before being poured over the master structure, where the liquid-phase PDMS conforms to the template's shape. Remaining air bubbles are removed through piercing with a thin syringe needle. The structure is then thermally cured, where silicon hydride groups present in the curing agent react with vinyl groups present in the base to form a cross-linked elastomeric solid. Afterwards, the PDMS is peeled off the master template. This process is critical as, upon

separation, cracks can appear in the polymer surface; to facilitate this process, the master template can be first silanized. The final structure replicates with high fidelity the features present in the master. Like in photolithography, the microfluidic components are formed at the PDMS surface, which requires an additional sealing process; however, this process is easier with polymers than with glass-based microfluidic channels. The device may be sealed reversibly or irreversibly against a PDMS, silicon or glass cover. Reversible sealing may be performed in ambient laboratory conditions and is achieved by conformal contact (van der Waals contact) between the PDMS and the sealing layer. The PDMS surface is hydrophobic, meaning that the resulting device can be easily dismantled by washing it in water; this can be done multiple times without degradation of the polymeric layer. The PDMS surface can, however, be made hydrophilic by exposing it to an oxygen plasma, which generates silanol groups on its surface and destroys methyl groups. Therefore, if the microfluidic channel and cover glass/polymer are subjected to plasma treatment, and if both structures are brought in contact immediately after this procedure (in order to avoid surface reconstruction) the sealing is irreversible. Although this bonding approach is simpler than its equivalent in all-silicon or all-glass-based devices, it is important to note that the inlet and outlet ports need to be made in the cover layer prior to this procedure which can introduce some difficulties when aligning both substrates; these openings are made in a PDMS cover layer by punching holes at the desired locations. Other technical problems related to the polymer itself may also arise. The elastomeric character of PDMS can lead to adhesion and capillary forces, which exert stress on the elastomeric features and can create defects in the device and cause these features to collapse. PDMS also shrinks by a factor of 1% upon curing, which means it is not the best material for the production of high-aspect ratio structures, and swells in the presence of organic non-polar solvents.

Hot embossing is generally applied to thermoplastic materials, namely PMMA [79]. These materials consist of an unlinked or weakly linked linear chain of molecules. Above its glass transition temperature, the polymer becomes plastic and can be molded into a certain form that is maintained once the polymer is cooled below this temperature. In this process, PMMA, in solid state, is put in contact with the master template and both structures are placed inside a vacuum chamber, in order to prevent trapping of air bubbles inside the final device. The PMMA layer and master template are simultaneously heated to a temperature above the polymer's softening point (usually between 100°C and 180°C), so that the PMMA becomes malleable and adapts to the features of the master template; the polymer and master template should present similar thermal expansion coefficients to minimize thermally induced stress in the final structure. The system is then cooled down so that the PMMA substrate can solidify, before being peeled off the master template. Like in the previous case, the channel is formed at the polymer's surface and, therefore, an additional bonding step (against glass, silicon or PDMS cover) is necessary to seal the device. For thermoplastics, adhesive or thermal fusion bonding are commonly employed. Solvent bonding can also be used, where a solvent is introduced in both substrate's surfaces which makes the polymer chains mobile, leading to extensive intertwining of

chains between both surfaces and resulting in a strong bond. The cover layer contains the openings for inlet/outlet connections.

Injection molding can also be used to fabricate microfluidic channels in PMMA [79]. The master template is placed inside a chamber with an inlet for injection of polymer pellets. By applying high pressure and high temperature (above the glass transition temperature of PMMA), the polymer pellets melt and conform to the features of the master structure. The entire system is then cooled and the PMMA solidifies on top of the template. Afterwards, the PMMA is separated from the master structure and sealed, using the same procedure as for hot embossing.

Besides their low cost, micromolding techniques allow rapid and easy prototyping of devices, and facilitate the demonstration and testing of new concepts. The use of polymers also avoids some problems related to the use of hard materials (formation of sharp shards on breakage) and enables the production of active components (e. g. valves and pumps). Still, the fabrication is restricted to the polymer surface, which hampers the production of 3D devices. Like in photolithography, these have to be fabricated by stacking two-dimensional planar layers, which increases the process complexity and limits some of the main advantages of these techniques, namely their simplicity and low fabrication time. Additionally, integration of microfluidic systems with electrical or optical components in a single substrate is challenging. Although hybrid devices, where a polymeric layer containing the microfluidic channels is bonded to a silicon/glass substrate containing the optical or electrical components, can be assembled, this option restricts the geometrical design of the device.

2.1.2 Integrated Optics in Glass

Although many optical materials can be employed in the fabrication of photonic integrated circuits, here, the focus is solely on integrated optics in glass. Indeed, glass still remains a fundamental material due to its excellent transparency and high threshold to optical damage. Further, it provides a relatively wide interval of refractive indices to choose from, and can be easily doped with active and functional ions, elements or compounds for added functionality. Additionally, glass is a fundamental component in the main technological platforms for photonic integrated circuits, namely silica-on-silicon and silicon-on-insulator.

The design of photonic integrated circuits relies on the fabrication of optical waveguides, whose most basic requirement for light confinement is that the guiding layer has a refractive index higher than the surrounding media. The increase of the refractive index can be triggered by several techniques, illustrated in figure 2.3. These can be divided in two categories: physical or chemical deposition of a thin film of higher refractive index than the underlying material, or localized modification of the refractive index of the glass. In particular, FHD (flame hydrolysis deposition), PECVD (plasma-enhanced chemical vapour deposition) and ion exchange in glass are mature technologies which have led to the production of high-quality low-loss passive components for optical communication systems and optical interconnections [80, 81, 82]. In FHD and in PECVD,

SiCl_4 and GeCl_4 vapours fed into a vacuum chamber react with flowing oxygen, and form SiO_2 and GeO_2 soot that deposits on top of the glass substrate. Meantime, ion exchange is based on the substitution of an ion initially present in the glass (usually Na^+) with another ion (e.g. Ag^+ , K^+ , or Li^+) supplied from an external source. These processes are followed or complemented by photolithography and reactive ion etching to pattern the waveguiding path. Another low-cost and versatile approach is that of sol-gel processing, which is based on the hydrolysis and condensation of metal alkoxides, and offers a viable route to the preparation of thin film optical waveguides on every kind of glass and composite.

Despite the maturity of planar lightwave circuit technology, the presented techniques still show some limitations. The design of photonic integrated circuits in a 3D geometry is cumbersome; additionally, in FHD and PECVD, the cross-section of the optical waveguides is restricted to a rectangular shape. Patterning of the optical waveguide also relies on photolithography and etching which is costly, complex and requires the use of cleanroom technologies.

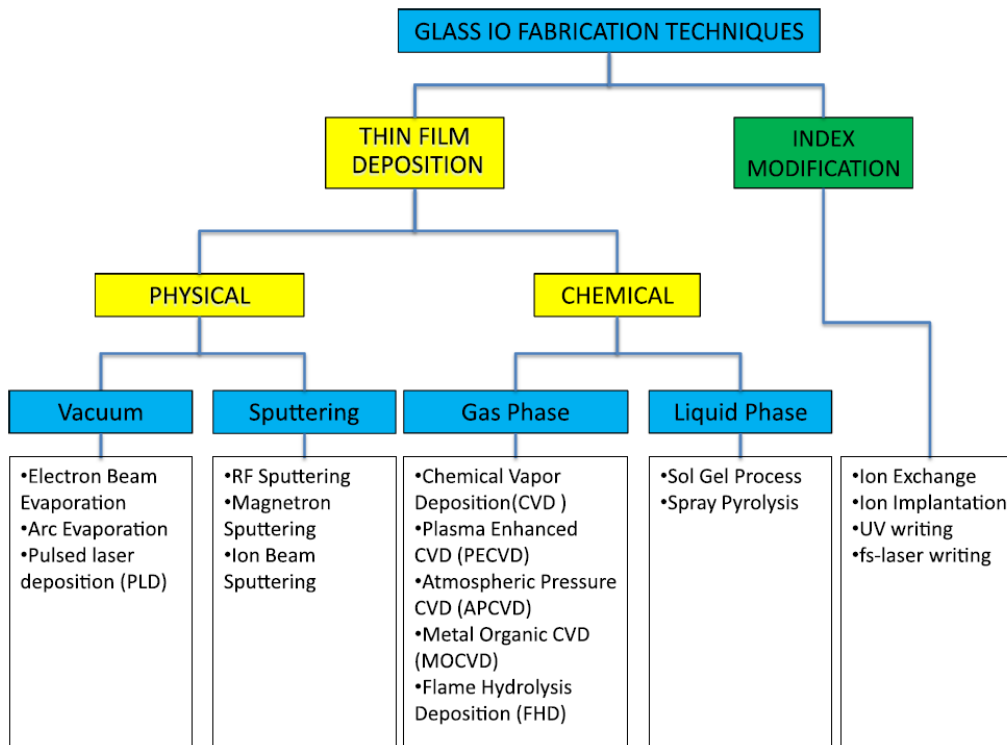


Figure 2.3: Typical fabrication techniques of glass optical waveguides, divided in two major categories: deposition of thin films of higher refractive index than the underlying layer and localized modification of the refractive index of the host material. Image was taken from [82].

2.2 Fs-Laser – Transparent Material Interaction

2.2.1 Non-Linear Absorption and Ionization Mechanisms

Glasses are transparent over a wide wavelength range, which spans from the visible to the near-infrared spectrum. Fused silica, for instance, is optically transparent from

around 250 nm to 2000 nm. Accordingly, the energy of an incident laser pulse, operating within this wavelength range, cannot be linearly absorbed by these media. Instead, the laser energy is absorbed through non-linear mechanisms [83, 84, 85]. Still, for non-linear absorption to occur, the electric field strength of the laser pulse must equal the electric field strength that binds the valence electrons in the atoms ($\simeq 10^9$ V/m), which corresponds to laser intensities around 5×10^{20} W/m² [86]. Such high intensities can only be achieved by either: (i) increasing the pulse energy, (ii) using ultrafast lasers with ultrashort pulse duration, or (iii) decreasing the beam's focal spot size through linear focusing with an objective lens or through self-focusing due to the optical Kerr effect [4, 87].

Unlike linear absorption, non-linear absorption is confined to the focal volume since only within this region is the laser intensity high enough to drive this process [4, 86], as illustrated in figure 2.4. Further, this requirement means that the absorption is not limited to the material's surface. In fact, the ability to micromachine the interior of the material, without affecting its surface, and to localize the material transformation to a submicrometric volume (minimum volume reported of 0.008 μm^3) seems to be a unique characteristic of ultrafast laser direct writing [86].



Figure 2.4: Comparison of the modified volume through linear and non-linear absorption. Image was taken from [88].

There are two main mechanisms for non-linear absorption to proceed: photoionization and avalanche ionization, depicted in figure 2.5. Photoionization refers to direct excitation of an electron from the valence band to the conduction band through multiphoton ionization and/or tunnelling ionization [83, 85]. Tunnelling ionization, shown in figure 2.5(A), is described as a laser-induced suppression of the Coulomb well that binds a valence electron to its parent atom, thus facilitating tunnelling of the bound electron through the shorter barrier. As shown in figure 2.5(C), multiphoton ionization is characterized by the simultaneous absorption of several photons by an electron, which is promoted to the conduction band if the absorbed energy equals or surpasses the material's bandgap energy (E_g), *i.e.* if $k\bar{h}\omega \geq E_g$ where k is the minimum number of photons that satisfy this relation, $\bar{h}$ is the Planck constant, and ω is the angular frequency of the laser beam. Notice that this process requires multiple photons, as the energy of a single photon is lower than the material's bandgap energy, and therefore not enough to promote transition to the conduction band.

The occurrence of each regime can be predicted by the Keldysh parameter (γ),

according to the following equation:

$$\gamma = \frac{\omega}{e} \left[\frac{mcn\varepsilon_0 E_g}{I} \right]^{1/2} \quad (2.1)$$

where ω is the laser frequency, I is the laser intensity at the focus, m and e are the reduced mass and charge of an electron, respectively, c is the velocity of light in vacuum, n is the refractive index of the material, E_g is the bandgap of the material, and ε_0 is the permittivity of free space [83]. When $\gamma \gg 1.5$ photoionization is dominated by multiphoton ionization. Otherwise, when $\gamma \ll 1.5$, which is typically associated to pulses shorter than 10 fs, it is dominated by tunnelling ionization. In the intermediate regime, photoionization is a mixture of both processes as shown in figure 2.5(B) [83]. Multiphoton ionization dominates at weak laser intensities and/or high laser frequencies (low laser wavelengths), whereas tunnelling ionization predominates at strong laser intensities and/or weak laser frequencies (high laser wavelengths). Most reports work in a regime where γ is much larger than one, and, consequently, multiphoton ionization dominates the excitation process [85]. Within this dissertation, typical values for the pulse energy and beam radius are 100-200 nJ and 2-3 μm at the focus, respectively. Accordingly, for irradiation of fused silica at 515 nm (band gap between 8 and 9 eV [89, 90]), the Keldysh parameter is higher than 1.5 and photoionization is dominated by multiphoton ionization assisted by three-photon absorption.

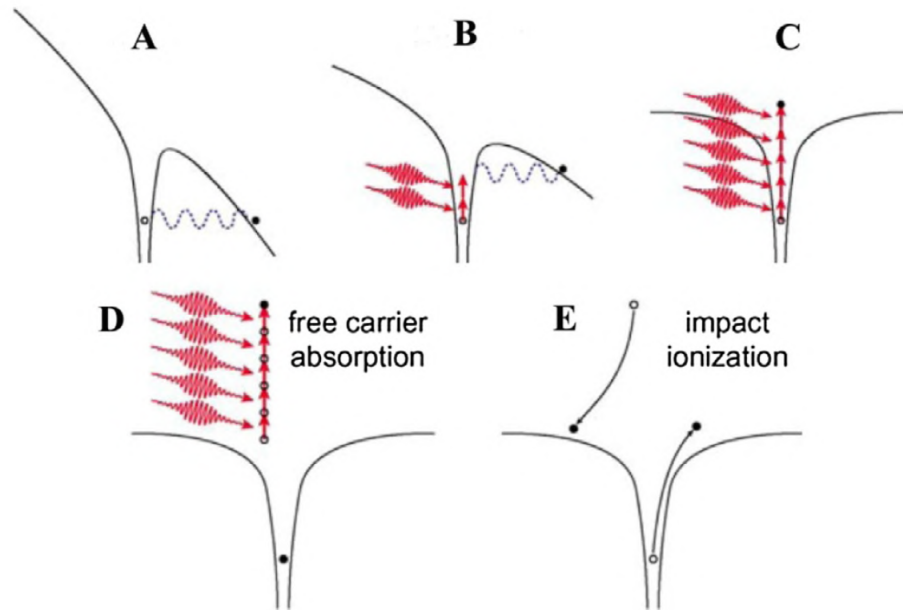


Figure 2.5: Depiction of the possible non-linear ionization mechanisms: (A) tunnelling ionization, (B) mixture of tunnelling and multiphoton ionization, (C) multiphoton ionization, and (D,E) avalanche ionization through free-carrier absorption and impact ionization. Image was taken from [83].

Electrons in the conduction band – free-carriers – may also absorb more energy and impact ionize electrons from the valence band to the conduction band [85]. The absorption can occur through two different phenomena, depending on the laser wavelength. In the near-ultraviolet range and visible (260-800 nm) absorption occurs via direct transition

between different sub-conduction bands, while in the near infrared-range (800-2000 nm) the free electrons absorb the laser energy through inverse bremsstrahlung (*i.e.* the free carrier directly absorbs energy from the incident laser beam) [83, 89, 91]. After absorption, if the free-carrier's energy exceeds the conduction band minimum by more than the material's bandgap energy, electron collisions can ionize another electron from the valence to the conduction band [83, 85], as shown in figure 2.5(D-E). As long as the laser field is present, the free-carriers, present in the conduction band, can regain kinetic energy through absorption and impact ionize another valence-band electron, resulting in an avalanche process where the free electron population exponentially increases [83, 85, 86]. The more collisions there are, the more efficient is this process. The density of electrons in the conduction band (N) grows according to:

$$\frac{dN}{dt} = \eta N + \sigma_k N I^k \quad (2.2)$$

The first term on the right-hand side of the equation accounts for the growth due to avalanche ionization, where η is the avalanche ionization rate which is a linear function of the laser intensity (*i.e.* $\eta = aI$, where a is a constant) [83, 85]. The second term corresponds to the photoionization rate, predicted by Keldysh, where σ_k is the multiphoton absorption coefficient for absorption of k photons. The validity of equation 2.2 is still under question as it does not consider the effect of pulse duration. Additionally, for dielectric materials such as fused silica, equation 2.2 also has to be modified to include free carrier losses (self-trapping and recombination), which may occur on a timescale comparable to the pulse duration [85].

As the density N increases, this collection of free electrons starts to behave as a strongly absorbing electron-ion plasma, which absorbs the laser energy through free-carrier absorption, thereby increasing its kinetic energy and temperature. The plasma oscillates at a frequency ω_p that grows with the carrier density N , according to the relation:

$$\omega_p = \sqrt{\frac{e^2 N}{\epsilon_0 m^*}} \quad (2.3)$$

where N is the carrier density, ϵ_0 is the electric permittivity (in vacuum), and e and m^* are the charge and effective mass of an electron respectively [85, 91]. When the plasma and laser frequency match, the plasma is said to be at critical density ($\simeq 10^{29} \text{ m}^{-3}$) [4, 83]. At this point, the plasma becomes strongly absorbing; still, not all the laser energy is absorbed due to optical losses during beam propagation and due to partial reflection by the plasma [84, 85, 89, 92].

Avalanche ionization requires an initial non-zero population of electrons in the conduction band in order to start [83, 89]. The provenience of the seed electrons depends on the laser pulse duration. For picosecond long pulses, the peak intensity is not high enough to efficiently cause photoionization. Consequently, avalanche ionization relies on the existence of either thermally excited carriers, ionized impurities or defect states. In turn, the threshold for avalanche ionization significantly depends on the number of impurities or defects in the focal volume, rendering the optical breakdown process non-deterministic [83, 93]. On the other hand, for laser pulses around 100 fs, because higher peak intensities can be obtained, avalanche ionization is seeded by free

carriers excited to the conduction band through photoionization processes, as has been numerically and experimentally studied in [89, 92]. Consequently, because avalanche ionization does not depend on the existence of defect or impurities within the material, optical breakdown is a more predictable and deterministic process [83, 86, 93]. For even shorter pulses (around 10 fs), photoionization may be enough to reach a sufficient plasma density for damage/modification [83]. Furthermore, focusing the fs-laser beam on the surface or bulk of the material also affects the absorption dynamics. Surface states or contaminants existent at the material's surface may provide seed electrons for avalanche ionization, thereby facilitating optical breakdown [83].

The extent at which both mechanisms, photoionization and avalanche ionization, dominate the growth of the density of free-carriers is also related to the material's bandgap. In low bandgap materials, non-linear photoionization may be enough to generate a critical plasma density to induce optical breakdown [83]. On the other hand, avalanche ionization plays a bigger role in high bandgap materials, such as fused silica [83, 86]. Moreover, the prevalent ionization mechanism also plays a role in the laser-induced structural modification [92].

2.2.2 Damage Mechanisms

Following the fs-laser induced electronic excitations, the free carriers transfer their energy into the lattice, thereby causing a local modification of the material's phase and structural properties [84]. Energy can be transferred through different routes, depending on the material's physical and thermal properties and on the irradiation parameters, with each one triggering a specific material transformation [90]. Here, the main mechanisms responsible for the laser-induced structural modifications observed in fused silica are highlighted [94].

In short, for fs-laser pulses, the deposition of the energy in the lattice involves two processes: (i) relaxation of the free electrons into self-trapped excitons, and (ii) recombination of the self-trapped excitons or formation of point defects [85]. The timescales associated to these events are shown in figure 2.6. Through carrier-carrier and carrier-phonon scattering (thermalization events) the free electrons transform into excitons, which are a bound state of electron-hole pairs attracted to each other by electrostatic Coulomb force. In wide bandgap materials, such as fused silica, the excitons and phonons (lattice vibrations) are strongly coupled, and the excitons further relax into self-trapped excitons. Self-trapped excitons are a means of converting electronic excitations into energetic atomic processes, which result in a permanent structural/phase modification of the irradiated material. This can occur either through formation of point defects or through recombination processes [84, 95, 96]. In fused silica, the time for free carriers to decay into self-trapped excitons is around 150 fs [84, 97, 98].

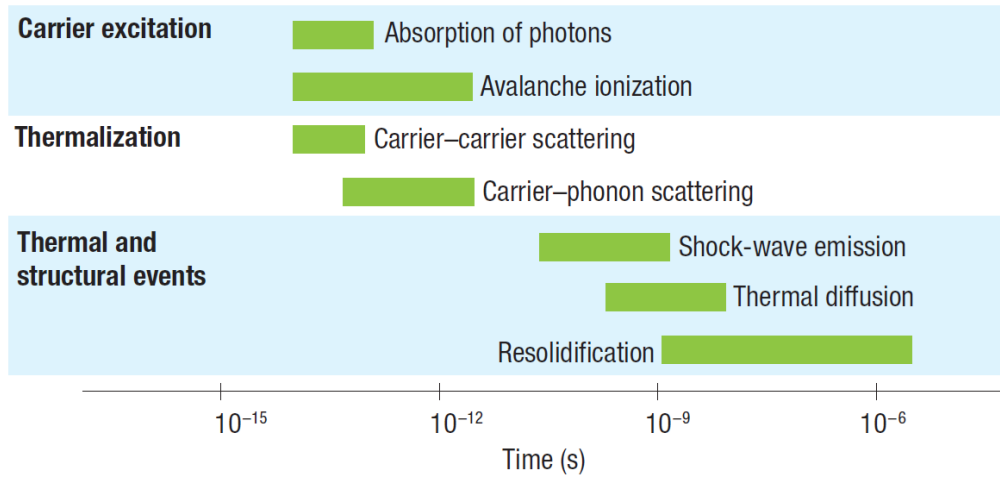


Figure 2.6: Timescale of the physical phenomena involved in the interaction between ultrafast laser pulses and transparent materials. Image was taken from [86].

Recombination of self-trapped excitons occurs in a nanosecond timescale, either through radiative or non-radiative mechanisms. Radiative recombination is associated to photon emission at discrete wavelengths, whereas non-radiative recombination involves coupling between the self-trapped excitons and the lattice vibrations. In the latter, the energy transferred to the lattice is converted into heat that can increase the temperature of the focal volume to near the glass' softening point. At these temperatures, thermodynamical processes, taking place in a timescale between 10^{-9} s and 10^{-6} s, can result in permanent structural changes within the fs-laser affected zone [86, 97, 99].

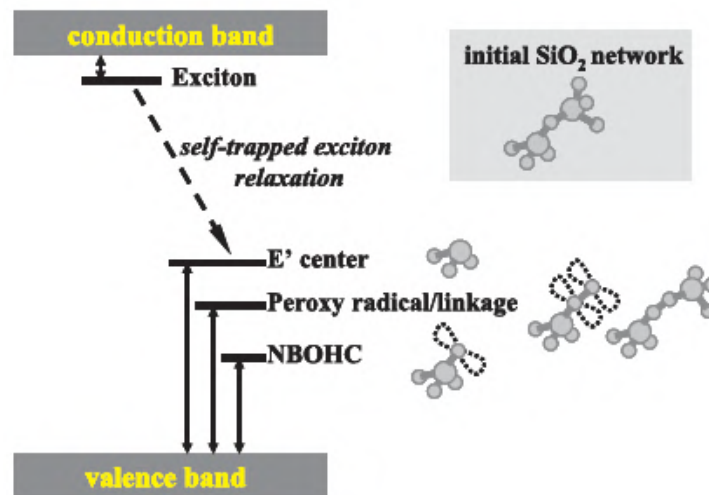


Figure 2.7: Decay of free-carriers into point defects, mediated by relaxation of self-trapped excitons. Image was taken from [85].

Although with a lower yield, self-trapped excitons can also relax into intrinsic point defects within the irradiated material [84, 85, 96, 100], as illustrated in figure 2.7. Amorphous fused silica is constructed from SiO₄ tetrahedrals, with silicon at its centre and an oxygen atom at each of the four corners. Self-trapping is accompanied by a strong distortion, in some cases even in rupture, of this structure. Weakening of the

Si–O–Si bond can lead to the removal of an oxygen atom from its equilibrium position in the tetrahedral arrangement, thereby provoking an arrangement of the atomic structure. Formation of NBOHC (non-bridging oxygen hole centre) states, oxygen deficiency centres (either ODC(I) and ODC(II)), peroxy linkage (Si–O–O–Si), peroxy radicals (Si–O–O) and silicon dangling bonds (SiE' centre) have all been reported through measurements of the photoluminescent spectrum and through Raman spectroscopy. These alterations in the atomic arrangement of the focal volume result in different physical and optical properties, in comparison to the pristine material. In fused silica, the decaying time of self-trapped excitons into point defects is around 400 ps [98].

2.2.3 Influence of Laser Parameters and Irradiation Conditions

Optical breakdown and subsequent structural modifications are only triggered when the pulse energy surpasses a threshold value (E_{th}). For diffraction-limited focusing on the presence of weak self-focusing, Schaffer *et al* [83] proposed the following empirical model which defines the threshold energy as:

$$E_{th} = \frac{I_{th}\tau\lambda^2}{\pi (NA)^2 + I_{th}\lambda^2/P_{cr}} \quad (2.4)$$

where I_{th} is the threshold intensity, τ is the laser pulse duration, λ is the laser wavelength, NA is the numerical aperture of the objective lens, and P_{cr} is the critical power for self-focusing. Further, the material's physical, optical and thermal properties and the exposure conditions also influence the spatial distribution of the deposited energy, which will influence the size and shape of the modified volume [84, 86]. Understanding how all these parameters impact the laser-induced modification is key to correctly design optical and microfluidic systems.

Laser Wavelength

According to equation 2.4, the energy threshold is influenced by the laser wavelength, with different behaviours being observed depending on the pulse duration [93]. For pulses longer than 10 ps, the damage is governed by avalanche ionization seeded by background carriers, and the energy threshold is nearly independent of the laser wavelength. As the pulse duration shortens (100-1000 fs), photoionization starts to induce avalanche ionization, with the prevalent ionization mechanism (multiphoton or tunnelling ionization) being determined by the laser wavelength, as studied by Keldysh through equation 2.1. For this range of pulse durations, the energy threshold increases linearly with the wavelength in the ultraviolet to visible range (260-800 nm), is constant in the near infrared range (800-2000 nm), and starts decreasing as the wavelength increases above 4700 nm [89]. In particular, within the ultraviolet to visible range (260-800 nm), Keldysh predicted the photoionization rate to decrease with increasing wavelengths which, in turn, means that the energy threshold increases with the wavelength [89, 93]. Both numerical and experimental results have further confirmed this prediction, by showing that the inscription threshold in fused silica is lower at 515 nm than at 1030 nm [87, 101]. For

extremely short pulses (<10 fs), tunnelling ionization becomes the dominant mechanism, and the energy threshold becomes independent from the laser wavelength again.

Moreover, for the same irradiated medium, higher laser wavelengths increase the number of photons (k) involved in multiphoton ionization, which further confines the modified volume and improves the spatial resolution. Assuming an incident fs-laser pulse with a spatial Gaussian profile, the absorbed energy profile will be proportional to the k^{th} power of the Gaussian distribution. Consequently, the modified volume narrows with increasing order of multiphoton absorption, as evidenced in figure 2.8. Nevertheless, although higher laser wavelengths can improve the spatial resolution, it may also result in a less efficient deposition of energy due to lower photoionization rates (see previous paragraph) [87]. The optical properties of the irradiated material, namely linear and non-linear refractive index, also influence the propagation of the fs-laser beam across it.

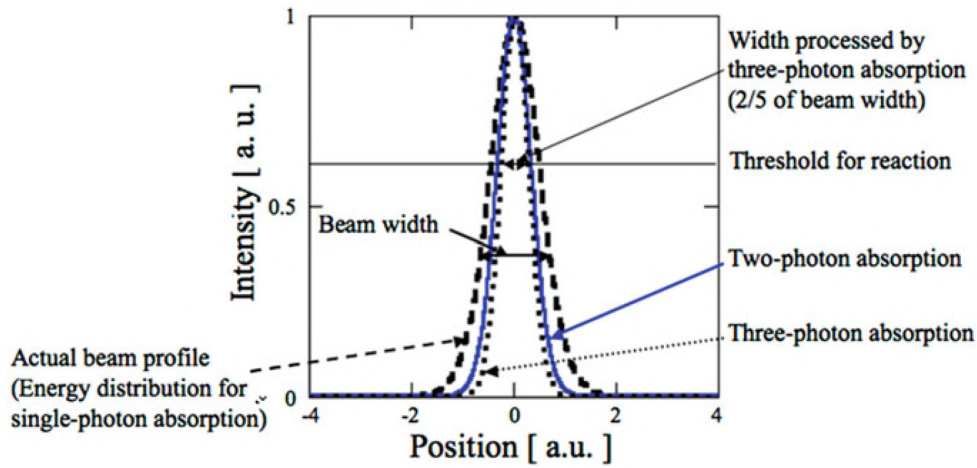


Figure 2.8: Beam profile (thick dashed line) and spatial distribution of laser energy absorbed by transparent materials through two (solid line) and three (thin dashed line) photon absorption. The solid horizontal line indicates the reaction threshold. Image was taken from [102].

Pulse Duration, Repetition Rate and Scanning Speed

The dynamics of the fs-laser induced modification also varies if the sample is exposed to a single shot or to a train of laser pulses (temporally separated by the inverse of the laser repetition rate), or if the sample is kept static or scanned across the fs-laser beam focus.

For static exposure and multiple pulse irradiation, the energy threshold depends on the pulse duration (τ). For an 800-nm fs-long laser beam with repetition rate of 100 kHz focused inside a fused silica substrate, Poumellec *et al* [84] determined two baseline thresholds depending on the pulse duration. Pulse durations between 40 and 170 fs revealed a constant threshold energy of 40 nJ, whereas longer pulse durations ranging from 170 to 500 fs showed a higher threshold of 80 nJ. Meanwhile, with pulses longer than 10 ps, the energy threshold scales as $E_{th} \propto \sqrt{\tau}$.

If the sample is translated across the laser beam, it becomes important to consider the net fluence, which defines the deposited energy per unit area. This parameter is proportional to the ratio between the laser repetition rate and the scanning speed, with an increase in the translation velocity resulting in a lower number of incident pulses per unit area and in a consequent decrease of the deposited energy [101]. Further, this relation also shows that the net fluence only depends on the ratio between the former parameters. In the context of microfabrication, this means that, as long as this ratio is kept constant, the scanning speed can be increased (or the fabrication time can be shortened) without affecting the resultant modification [97].

Considering single-shot exposure, different regimes may also be observed if the pulse duration is higher or lower than the electron-phonon coupling time (around 150 fs in fused silica [98]) as shown in figure 2.9. For fs-laser irradiation, the energy is deposited in the lattice only after the pulse is gone [83, 86]. The non-linear absorption and the thermalization (and subsequent) processes are then said to be decoupled. Consequently, this results in minimum heat diffusion outwards of the focal area, and in the absence of heat-affected zones and collateral damage [85, 96, 99]. Therefore, the modified volume roughly matches the focal one (in the absence of self-focusing), which enables micromachining with high precision [86, 103]. Further, the irradiation proves to be a deterministic and repeatable process. Meanwhile, for pulses longer than a few tens of picoseconds, thermalization and structural and thermal events take place while the laser pulse is still active [83]. In turn, heat builds up within the focal volume, before radially diffusing outwards. The energy is then deposited in the lattice through thermal events, which results in a delocalized breakdown process and in an expansion of the modified volume.

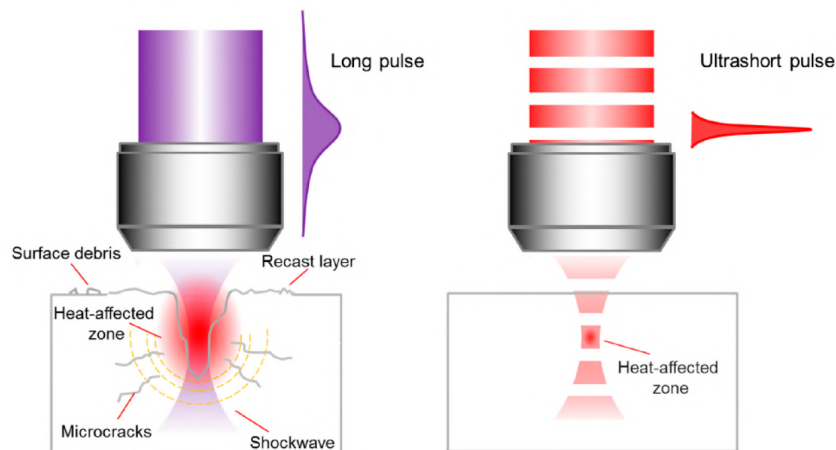


Figure 2.9: Comparison of the effect of long and ultrashort pulses on the size of laser-modified material. Image was taken from [104].

A similar effect can occur depending on the relation between the laser repetition rate and the material's thermal diffusion time. If the repetition rate is low enough, such that the

time interval between pulses is bigger than the material's thermal diffusion time, then all pulses can be thought of acting independently from one another. In other words, all thermal and mechanical relaxation processes are completed before the next pulse arrives. Nevertheless, incubation and cumulative effects cause a slight reduction of the energy threshold, in comparison to the threshold for single-shot exposure [4, 83, 105]. For high repetition rates, where the time interval between pulses is lower than the material's thermal diffusion time, heat builds up in the focal volume and the structural modification is the result of thermal processes [4, 96]. The model proposed in [97] shows that, in this regime, the temperature in the focal volume never decreases to below the material's working point before the next pulse arrives. Consequently, during exposure, heat is accumulated within the irradiated volume, leading to localized melting after the pulse train is gone, which is then followed by rapid cooling and resolidification [83, 97]. In fused silica, where the thermal diffusion time is 1 μs [97], thermal effects are only meaningful for repetition rates above 1 MHz.

Still, the observation of thermal effects also depends on the laser pulse energy and on the thermal properties of the irradiated material. For instance, Eaton *et al* [97] concluded that thermal effects could be more easily triggered in borosilicate glasses than in fused silica due to the lower band gap and lower working temperature, 4 eV versus 9 eV and 1100°C versus 1800°C, respectively. In turn, a combination of high repetition rate (>1 MHz), high pulse energy ($> 1 \mu\text{J}$ to increase the temperature of focal volume past the working temperature) and low laser wavelength (to improve efficiency of non-linear absorption) is needed to trigger these effects in fused silica [106]. Although thermal effects can mitigate the formation of cracks and/or of rougher features within the modified volume, it is also argued that they warrant a worse spatial resolution in comparison to single-shot exposure or to irradiation with low repetition rates [4, 86].

Beam Polarization

Although not explicit in the equation above, the energy threshold for laser-induced damage also depends on the polarization of the fs-laser beam. For an 800-nm and 120-fs long pulse, focused inside a fused silica substrate, Little *et al* [7] observed that the energy threshold for laser-induced damage is lower for linear polarization when the peak irradiance is lower than 42 TW/cm^2 , while for higher peak irradiances the threshold is lower for a circularly-polarized beam. These results were explained by noting that the cross-section of 6-photon ionization, and therefore the photoionization rate (described through the first term of the right-hand side of equation 2.2), is higher for linear polarization when the peak irradiance is lower than 42 TW/cm^2 , and that it becomes higher for circular polarization when the peak irradiance surpasses the latter value [7, 84]. Also, when translating the substrate across the focus of a linearly polarized laser beam, the threshold energy was found to be the same regardless if the beam's polarization was parallel or perpendicular to the scanning direction [7, 8].

“Quill” Effect

By scanning a fused silica substrate in a plane orthogonal to the direction of propagation of the fs-laser beam, Kazansky *et al* [106] observed that the characteristics of the laser-induced damage would depend on the scanning direction. This directional dependence – denominated “Quill” effect – manifests itself through a variation in the birefringence, roughness/texture and, to a lesser degree, in the dimensions of the laser-affected zone when scanning the sample in the forward or reverse direction [107]. This effect is explained through a tilt in the pulse front, generated due to frequency chirp and enhanced by the electron-ion plasma, which creates an intensity gradient across the beam profile. In the presence of this gradient, ponderomotive force expels the free carriers away from the focal spot along the direction of the pulse front tilt. By translating the substrate along the direction of the pulse front tilt, the ponderomotive force will trap and displace the free carriers along the scanning direction, thereby affecting the oscillation of the plasma and subsequent structural modifications of the irradiated medium. If the scanning direction is reversed, trapping of the free electrons ceases to be observed. Still, this effect is only observed at a sufficiently high free carrier density (and high plasma temperature), which is attainable either by increasing the pulse energy (>800 nJ) or by decreasing the scanning speed (<500 $\mu\text{m/s}$) [106, 107].

Numerical Aperture of Focusing Objective

As predicted by equation 2.4, the energy threshold is higher for lower numerical apertures [86]. In fact, Poumellec *et al* [84] observed that the energy threshold is proportional to $\text{NA}^{-1.9}$ if the numerical aperture is higher than 0.3-0.4 (in accordance with equation 2.4), whereas for lower numerical apertures the threshold scales with $\text{NA}^{-0.8}$.

2.2.4 Propagation of Gaussian Laser Beams

Linear Focusing

High laser peak intensities are required to drive non-linear absorption, which is typically obtained by focusing the fs-laser beam inside the material. For linear propagation and by neglecting aberrations, the intensity distribution ($I(\rho, z)$) of a Gaussian beam can be described by:

$$I(\rho, z) = \left(\frac{\omega_0}{\omega(z)} \right)^2 \exp \left(-\frac{2\rho^2}{\omega^2(z)} \right) \quad (2.5)$$

where r is the radial distance, z the axial distance from the beam waist, ω_0 the waist radius, and $\omega(z)$ the waist radius along the beam propagation direction ($\vec{z}$). The waist radius along the beam propagation direction $\vec{z}$ is given by:

$$\omega(z) = \omega_0 \sqrt{1 + \left(\frac{z}{z_0} \right)^2} \quad (2.6)$$

where z_0 is the Rayleigh range defined as the distance from the beam waist where the beam radius increases by $\sqrt{2}$. The beam waist radius (ω_0) and the Rayleigh range (z_0)

are further defined as:

$$\omega_0 = \frac{M^2 \lambda}{\pi \text{NA}} \quad (2.7)$$

$$z_0 = \frac{M^2 n \lambda}{\pi \text{NA}^2} \quad (2.8)$$

where M^2 is the beam quality factor, λ the laser wavelength, and NA the numerical aperture of the focusing lens. In the absence of thermal effects and self-focusing, the volume of the laser-induced modification is close to the focal volume. Therefore, the width and height of the laser-affected zone can be estimated as twice the beam waist and twice the Rayleigh range, respectively [86]. Note that the ratio between the width and height $\frac{2\omega_0}{2z_0}$ equals $\frac{\text{NA}}{n}$. Accordingly, if the numerical aperture of the focusing lens is lower than the medium's refractive index, the cross-section is asymmetrical and elongated along the vertical direction [86, 106].

Optical aberrations, in particular spherical and chromatic aberrations, introduce some deviations to the intensity distribution. Chromatic aberrations are caused by the dispersion characteristics of the focusing lens, which fails to focus different wavelengths at the same convergence point. With a dry spherical lens, the refractive index mismatch at the air-substrate interface also leads to spherical aberrations which reduce the peak intensity near the focus and worsen the fabrication's spatial resolution. These aberrations are characterized by the beam failing to converge to a unique focal spot, due to an increase in the refraction of light rays that strike the lens near its edge, in comparison to the rays near the centre of the lens [32]. This effect is aggravated with higher numerical aperture lenses or when focusing at greater depths, and can be corrected by employing aspherical lenses or oil-immersion lenses, respectively [83].

Non-Linear Focusing

The high laser peak intensities ($I(\rho, z)$) necessary to trigger non-linear absorption, may also influence the propagation of the fs-laser beam within the material [94]. The refractive index of fused silica (n) is given by:

$$n = n_0 + n_2 I(\rho, z) \quad (2.9)$$

where n_0 and n_2 are the linear and non-linear refractive indices, respectively [83, 85]. Given that fused silica is a centrosymmetric material, the non-linear refractive index is expressed as:

$$n_2 = \frac{3\chi^3}{4\varepsilon_0 c n_0^2} \quad (2.10)$$

where χ^3 is the third-order non-linear electric susceptibility, ε_0 is the electric permittivity in vacuum, and c is the speed of light in vacuum. In fused silica, the non-linear refractive index is positive, and equals $3 \times 10^{-20} \text{ m}^2/\text{W}$ at 515 nm [92, 103]. Accordingly, the refractive index becomes higher at the centre of the beam in comparison to its wings, and the sample acts as a converging lens that further focuses the beam [83]. This effect, called self-focusing, dominates over diffraction when the laser power surpasses the critical

power (P_{cr}), defined as:

$$P_{cr} = \frac{3.77\lambda^2}{8\pi n_0 n_2} \quad (2.11)$$

In fused silica, the critical power is 0.9 MW for irradiation at 515 nm. If the optical power surpasses this value, the beam is expected to collapse. However, because the ionized plasma has a negative non-linear refractive index, it acts as a diverging lens and counters the effect of self-focusing [85]. Consequently, balancing between the positive Kerr effect and the plasma defocusing, turns the beam propagation similar to that of a soliton, resulting in the formation of one or more filaments that elongate the modified volume [87, 92, 103]. This type of propagation is preserved until the beam's power decreases to below the critical power for self-focusing, with filaments as long as 1 mm having been reported in fused silica [90]. Self-focusing occurs more easily when focusing with low-numerical apertures as it is necessary a higher energy to compensate for the larger focal volume and, consequently, to reach the threshold intensity. Contrarily, filamentary propagation can be prevented at tight-focusing conditions (higher numerical aperture) or with shorter pulses, because the energy threshold for damage is lower and the critical power for self-focusing is independent of the latter parameters [83, 84, 108]. Liu *et al* [108] also observed that the non-linear electric susceptibility (χ^3) of fused silica, and consequently the non-linear refractive index, depend on the polarization state of the incident fs-laser beam. They reported that the χ^3 of fused silica is higher for linear polarization than for circular polarization, which means that the critical power (and pulse energy) for self-focusing is lower for a linearly polarized beam. In addition, at sufficiently high intensities, self-focusing can occur before the beam reaches its focal position, which causes the head of the laser-induced damage to move upstream of the beam's propagation direction [103]; this displacement was in fact found to increase with the pulse energy [90, 92]. Other non-linear phenomena such as self-phase modulation, which is known to cause spectral broadening and for the laser pulses to acquire a frequency chirp, may also occur and affect the propagation of the laser beam and its interaction with the transparent medium [85, 90].

2.3 Fs-Laser Irradiation of Fused Silica

Exposure of fused silica to a fs-laser beam can result in three main modifications of relevance to micromachining: (i) localized isotropic increase of the refractive index [1], (ii) formation of birefringent and anisotropic structures named nanogratings [32, 109], and (iii) formation of sub-micrometric voids [94, 99, 109].

Typically, these regimes appear consecutively as the laser fluence increases. By focusing a pulse train, delivered by a Ti:sapphire laser system operating at 800 nm with a pulse duration of 100-150 fs and repetition rate of 100 kHz, inside a fused silica substrate with a 0.65NA lens, several authors determined the pulse energy range for each effect [4, 92, 99, 110]. Below 40 nJ, which defines the onset for optical breakdown, no damage was observed. In-between 40 and 150 nJ, fs-laser irradiation led to a smooth and

isotropic increase of the refractive index. Formation of nanogratings was seen for pulse energies between 150 and 500 nJ, whereas voids appeared at pulse energies higher than 500 nJ. The energy threshold for each modification slightly changes in silica-doped glasses [92, 95]. In particular, doping with germanium or phosphorus led to a decrease in the minimum energy necessary to observe nanogratings, while doping with fluor increased the energy threshold.

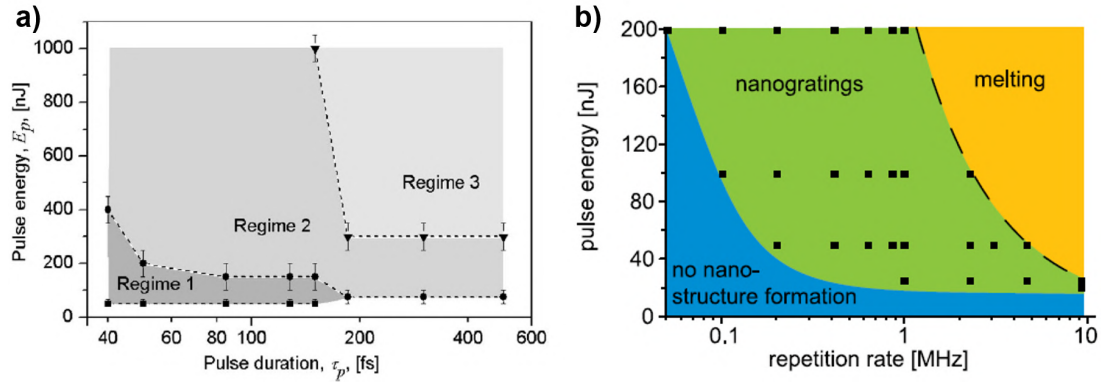


Figure 2.10: Processing window for each laser-induced modification observed in fused silica, against (a) pulse duration and (b) repetition rate. Image (a) was taken from [110], and image (b) from [105].

Still, the processing window for each regime depends on the parameters of the pulse train and on the focusing conditions [4, 84, 94]. For instance, figure 2.10(a) shows how it depends on the pulse duration [110, 111]. For pulse durations shorter than 150 fs, the threshold for isotropic increase of the refractive index is independent of this parameter, while the minimum energy for formation of nanogratings asymptotically decreases as the pulse duration elongates before plateauing at around 50 fs. Meanwhile, the threshold for formation of voids gradually decreases as the pulse duration increases. For pulses longer than 150 fs, the processing window for both the isotropic increase of the refractive index and the formation of nanogratings starts narrowing. Moreover, above a specific pulse duration, both modifications become indistinguishable from one another [84, 111]. This pulse duration depends on the numerical aperture of the focusing objective, with Hnatovsky *et al* [110] having determined it to be 200 fs for irradiation with a 0.6NA lens. According to figure 2.10(a), the minimum energy for formation of nanovoids is independent of pulse duration for pulses longer than 150-200 fs.

The threshold for refractive index change is also lower for multiple pulse exposure than for single-shot irradiation, due to incubation and cumulative effects [100]. Similarly, as illustrated in figure 2.10(b), the minimum pulse energy for the formation of nanogratings decreases as the repetition increases, before turning constant above 1 MHz [105]. However, this trend is accompanied by a continuous decrease of the upper energy limit and by shrinkage of the processing window, as a result of heat accumulation effects that become more meaningful as the repetition rate increases [105, 107, 112]. Still, nanogratings were observed in fused silica even when writing with repetition rates as high as 9.4 MHz [105].

All of these regimes have been confirmed for a wide range of numerical apertures, ranging from 0.4 to 0.75 [33]. Further, the minimum pulse energy to observe any of these effects increases opposite to the numerical aperture [33, 84].

In the remainder of this section, the main results regarding the morphology, composition and structural properties that define each modification are reviewed, as well as the respective formation models. A more thorough discussion can be found in [94, 100].

2.3.1 Isotropic Increase of the Refractive Index

The first mention of fs-laser induced increase of the refractive index, confined to the focal volume of glass substrates, was made by Hirao *et al* in 1996 [1]. Through micro-ellipsometry and/or refractive near field profilometry, this modification was described as an isotropic increase, along a step-index profile, of the refractive index of the modified volume relative to the pristine material [1, 86, 101], as is demonstrated in figure 2.11. Typical values of the laser-induced refractive index contrast range from 10^{-4} to 10^{-2} , which depends on the amount of energy absorbed by the material from the fs-laser beam and can be controlled through the exposure conditions, in particular through the pulse energy and scanning speed [101]. Similarly, tuning of the laser wavelength and/or of the beam polarization can enhance the photoionization rate and, consequently, increase the refractive index contrast. A stronger absorption is observed by irradiating fused silica at 515 nm rather than at 1030 nm, due to the ionization rate being higher for lower-order multiphoton absorption processes [101]. Irradiation with a linearly polarized beam also resulted in a higher refractive index contrast for peak irradiances below 38-42 TW/cm², whereas circularly polarized irradiation proved to be more efficient above this threshold [7, 8]. AFM measurements further revealed that the cross-section of the modified region is homogeneous with an associated roughness of a few nanometres [32], whereas cross-polarized microscopy showed that this modification is isotropic with no traces of birefringence [103, 107]. Thermal annealing also revealed that this modification is not permanent. As the annealing temperature grows past 500°C, the refractive index contrast starts decreasing, before the modification itself completely disappears at 1100°C [107].

Several studies revealed the composition and atomic structure of the fs-laser irradiated regions. Raman spectroscopy showed a higher concentration of three- and four-member silicon-oxygen ring structures within the modified volume, in comparison to the pristine material where five- and six-member ring structures predominate [4, 7, 94, 100]. This is accompanied by a reduction of the inter-bonding Si–O–Si angles, and by a narrowing of the distribution of the dihedral angles of adjacent SiO₄ tetrahedrals composing the silica matrix [100]. Infrared spectroscopy also confirmed the change in the Si–O–Si bond angle [4]. These results suggest compaction of the glass matrix and material densification [7, 94, 100]. Further, a linear relation between the refractive index and the concentration of three-member rings has been determined, with both quantities increasing with the irradiated dose before saturating [94, 100].

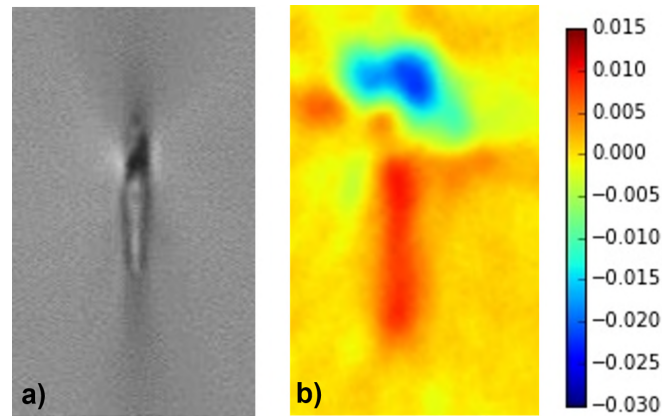


Figure 2.11: (a) Cross-section of fs-laser written optical waveguide and (b) associated refractive index profile. The brighter region of image (a) is related to an isotropic increase of the refractive index of 0.010-0.015.

Complementary ultraviolet and electronic spin spectroscopy also revealed the existence of point defects, namely SiE' centres, NBOHC and peroxy radicals, uniformly spread over the irradiated volume [1]. Similar conclusions were drawn from the luminescence spectrum, where a preferential generation of NBOHC was observed [94]. Moreover, the photoluminescence spectrum already indicated the presence of these defects after single-shot irradiation, but without visible refractive index changes [100].

Both thermal and non-thermal mechanisms have been proposed to explain these results and the observed structural modification [4, 86, 100]. In the fictive temperature model, non-radiative recombination causes the lattice to heat to a temperature above the material's softening point, which is followed by fast quenching where the irradiated focal volume freezes in a higher density state relative to its surroundings [4, 95, 96, 100]. However, this theory was debunked given that the concentration of free carriers is not enough to drive the temperature above the material's softening point during electronic relaxation and to induce melting of the glass network [94]. Moreover, the results obtained through Raman spectroscopy do not agree with the predictions made by this model, and this modification is also visible at repetition rates lower than a few MHz where no thermal effects occur [100].

Non-thermal mechanisms consider the refractive index change to occur due to densification resulting from defect-induced structural network reorganization [100]. Here, fast electronic relaxation (< 1 ps) via self-exciton trapping and Si–O bond breaking leads to the formation of point defects, in particular NBOHC, which promote the rearrangement of the silica matrix into a denser packing. As suggested by the experimental results, this transformation can occur at low temperatures and is dependent on the irradiated dose [100]. Further, this model is consistent with the observations that multiphoton ionization is enough to cause this modification [92]. For now, densification mediated by point defects seems to be the prevalent model to explain the formation of an isotropic region of higher refractive index. However, other non-thermal mechanisms, such as generation of colour centres or compaction and rarefaction after pressure wave release, have also been proposed to explain this modification [4, 86, 100].

2.3.2 Birefringent Refractive Index Change and Nanogratings

Between 1999 and 2002, several anomalous phenomena were reported and associated to an anisotropic structure formed in the bulk of fused silica after fs-laser irradiation [103, 113, 114]. Experimental observations of anisotropic scattering, anisotropic light reflection, and from birefringence through cross-polarized or Nomarski-DIC microscopy were all documented during this time period.

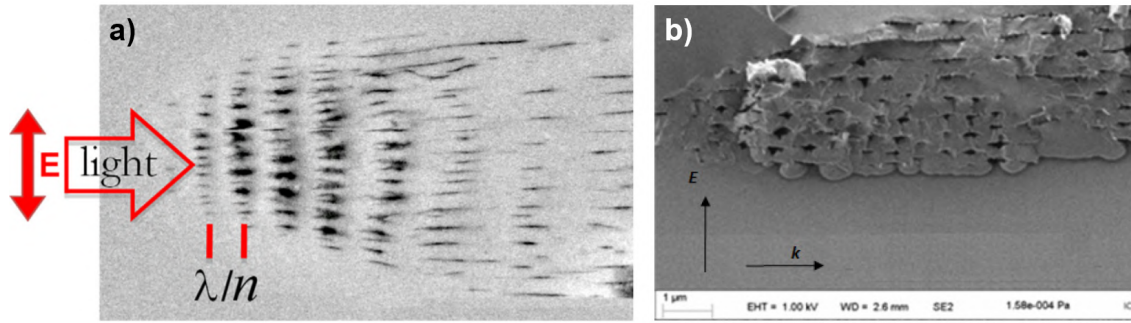


Figure 2.12: SEM image of the cross-section of a nanograting directly after fs-laser irradiation on a fused silica substrate, revealing the two distinct periodicities. k and E correspond to the direction of propagation and to the direction of polarization of the fs-laser beam, respectively. In both images, the fs-laser is incident from the left and the beam is polarized orthogonally to the scanning direction. Image (a) was taken from [115], and image (b) from [116].

Only in 2003, were these results associated to the formation of nanogratings [91], whose cross-section is shown in figure 2.12(a-b). If a fused silica substrate is irradiated by a linearly polarized fs-laser beam, these laser-induced structures are composed by a periodical modulation of thinner lower density layers alternating with higher density layers of weakly-modified fused silica. The refractive index of the less dense layers (n_1) is lower than the pristine's refractive index, and can reach a maximum contrast of 0.2 [96, 107, 109, 112]. Meanwhile, the refractive index of the higher density layers (n_2) is slightly higher than the pristine's refractive index. This pattern is distributed over the modified volume, with its cross-section presenting two distinct periodicities: a period Λ_k longitudinal to the direction of light propagation, while a transversal one Λ_E is aligned along the polarization of the fs-laser beam. As a rule of thumb, these periods scale with λ/n and $\lambda/2n$, respectively, where λ is the laser wavelength and n is the pristine material's refractive index. Further, the period Λ_E depends on the number of incident pulses [105], while it is independent of pulse duration [107, 110, 112].

Richter *et al* [105] have studied the formation of these periodic structures against the number of incident pulses, for a linearly polarized incident beam. During the first tens of pulses, they observed that the structures were already aligned perpendicular to the fs-laser beam's polarization, but irregularly distributed and with heterogeneous dimension. Only after around 500 pulses, were the nanostructures regular and periodic, with no vacancies in-between. Still, the period Λ_E kept reducing by increasing the number of incident pulses, until a saturation value was obtained. The number of incident

pulses needed to reach this saturation point decreased for exposure with higher pulse energies. Generally, both periods oscillate between 150 and 300 nm, while the filling factor (f) – ratio between the thickness of the less-dense layers and the period Λ_E – fluctuates between 0.1 and 0.4 [107, 112]. By scanning the glass substrate in relation to the fs-laser beam, the long-range order is preserved, which enables the fabrication of continuous nanogratings over a volume much higher than the focal one. This spatial coherency has been attributed to a self-replication technique underlying the formation of nanogratings [32].

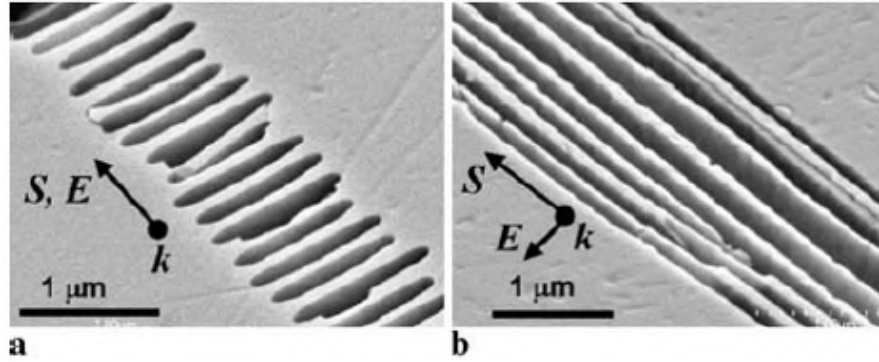


Figure 2.13: Top view image of nanogratings after chemical etching with the polarization of the incident laser beam (a) parallel and (b) perpendicular to the scanning direction, revealing their preferential alignment orthogonal to the laser beam polarization. The vectors S , E and k correspond to the scanning direction, to the polarization direction of the linearly polarized fs-laser beam and to the direction of propagation of the incident beam, respectively. Image was taken from [32].

These structures behave as a uniaxial negative birefringent material, where the polarization of the fs-laser beam solely defines the optical axis [95, 107, 112], as demonstrated in figure 2.13. In fact, regardless of the scanning direction and for a linearly polarized laser beam, the periodical modulation (Λ_E) and the optical axis are always oriented parallel to the beam's polarization [32, 103]. The strength of the laser-induced form birefringence can be controlled through the periodicity and material composition of the microstructure and, in turn, by the processing parameters [111]. Through an interferometric phase-stepping technique [107, 109], expressions for the extraordinary (n_e) and ordinary (n_o) refractive indices have been determined:

$$n_e = \sqrt{\frac{n_1^2 - n_2^2}{fn_2^2 + (1-f)n_1^2}} \quad (2.12)$$

$$n_o = \sqrt{fn_1^2 + (1-f)n_2^2} \quad (2.13)$$

As is the case for a negative uniaxial birefringent medium, the extraordinary refractive index (n_e) is lower than the ordinary refractive index (n_o), with typical values of linear birefringence ($B = |n_e - n_o|$) ranging from 10^{-3} to 10^{-2} [4, 91, 107].

When subjected to thermal annealing, the nanograting's refractive indices n_1 and n_2 start to converge towards the refractive index of the pristine medium as the annealing temperature increases from 500°C upwards, leading to a decrease of the

birefringence [107]. However, and contrary to the previously discussed modification, the nanogratings are still present even after thermal annealing at 1100°C, which suggests a permanent laser-induced modification [96, 107, 111]. Nevertheless, the orientation of the nanogratings can be re-defined if a fused silica substrate, already containing these structures, is again subjected to fs-laser direct writing over the existent modification [33, 111]. In that event, the pre-existent modification is erased, and new nanogratings aligned along the new polarization of the fs-laser beam are written.

The nanograting pattern can also vary according to the irradiation conditions. In particular, away from the thermal accumulation regime (<1 MHz) and for a linearly polarized incident beam, the pulse duration and energy affect its regularity [32, 33]. At low pulse durations (<130 fs) and relatively small energies (100-1000 nJ), the nanogratings are periodic, well-defined, weakly interconnected, and cover the full extent of the irradiated cross-section. As the pulse duration and/or pulse energy increases, the nanogratings enter a disruptive regime where the nanostructures expand both laterally and axially, become disordered and start to connect with each other. Further increase of pulse duration and energy past 300 fs and 1000 nJ, respectively, leads to an anomalous event, where the cross-section becomes conical and two site-specific material transformations occur [32, 95, 103, 105, 109, 112]. An irregular distributed network of nanocracks is formed at the rounder head of the modified volume, whereas its tapered tip exhibits a smooth modification consistent with the isotropic increase of the refractive index responsible for waveguiding [100, 107]. With a continuous increase of the pulse energy, the nanocracks start to fill the rest of the cross-section [96]. Meanwhile, if the fs-laser beam is circularly polarized, the nanostructures become randomly distributed [32].

Regarding the composition of the nanogratings, it is still a point of discussion among researchers [33, 96]. Canning *et al* [116] consider them to be nanoporous planes composed by decomposed silica and molecular oxygen ($\text{SiO}_{2(1-x)} + x\text{O}_2$). The nanopores are thought to be created from volume expansion resulting from Coulombic explosions at specific sites. Within the nanopores, strong Si–O bond breaking events caused by avalanche ionization result in molecular dissociation of highly ionized oxygen which recombine to produce dissolved oxygen that remains trapped within the pore, and in the formation of self-trapped excitons that relax into point defects, namely ODC centres and peroxy radicals [92, 96, 100]. This is in agreement with experimental observations. Raman spectroscopy shows that fs-laser irradiation produces molecular oxygen, in the form of free O_2 and dissolved O_2 within the silica network [96], while the photoluminescent spectrum reveals that ODC defects with one or two vacancies agglomerate within the nanopores [100]. At the same time, the formation of nanopores results in compressive stress in the layers surrounding them. This has been confirmed experimentally through Raman spectroscopy, which shows a decrease in the Si–O–Si bond angle and in an increase in the number of 3-membered ring structures, which point to densification of these intermediate regions [117, 118]. Meanwhile, Hnatovsky *et al* [32] have suggested that the narrow low-density layers are in fact photo-induced nanocracks. To reconcile both models, Champion *et al* [117] suggested that as the laser energy increases, the

stress accumulated within the material can be too high and can eventually relax and form randomly distributed cracks.

Several authors have also tried to explain the periodical alignment of the nanogratings. Shimotsuma *et al* [91] presented a model where bulk plasma waves, generated by the electron plasma, interfere with the electric field of the fs-laser pulse. The resulting interference pattern creates a periodic modulation of the plasma concentration orthogonal to the polarization of the fs-laser beam, with material transformation occurring only within the regions of high plasma concentration. This provokes the growth of periodic structures that freeze in the material after irradiation. Still, this theory predicts the temperature of the electron plasma to reach 10^7K , which implies a minimum pulse energy of $10\text{ }\mu\text{J}$ for nanograting formation that contradicts reported results where these structures developed with pulse energies around 100 nJ [32].

An alternative model, based on nanoplasmonic theory, has also been developed where the formation of nanogratings is a three-step process that requires multiple pulse irradiation (500-3000 shots) [32, 33]. First, the high non-linearity of light absorption and/or the presence of colour centres and defects causes inhomogeneous dielectric breakdown, and formation of randomly distributed spherically-shaped nanoplasmas. Due to a “memory” effect from previous shots, the threshold for multiphoton ionization is lowered within the nanoplasmas. Consequently, subsequent pulses increase the local ionization rate in these sites, and promote the growth of the nanoplasmas into nanoplanes along the direction of propagation of the fs-laser beam. Depending on the repetition rate, two different mechanisms have been proposed to explain this “memory” effect and why several pulses are needed to form nanogratings. For low pulse separations (between 500 fs and 1 ns) coupling between fs-laser pulses is mediated by self-trapped excitons, whereas for high pulse separations (between $5\text{ }\mu\text{s}$ and several milliseconds), the “memory” effect is due to the presence of (semi-)permanent defects, such as SiE' and NBOHC centres [98]. At the same time, Si-O-Si bond breaking, accompanied by formation of molecular oxygen and ODC centres, is restricted only to these nanoplanes [96]. With successive pulses, the electron plasma density inside them increases past the critical density, and the nanoplanes become quasi-metallic. In turn, they start interacting with the electric field of the fs-laser pulses, forcing them to self-organize into a periodical distribution throughout the focal volume. Although this model agrees with reported SEM and AFM profiles [96], and with experimental observations of the evolution of the nanograting period with the number of incident pulses [105], it requires a relatively high plasma density that contradicts directly measured values of plasma concentration.

Moreover, the previous model does not explain some finer features such as the two distinct periodicities. Another theory was advanced by Beresna *et al* [115], which considered the formation of nanogratings to be related to the interference of coherent exciton-polariton modes and recombination of self-trapped excitons. In particular, irradiation of a fused silica substrate with a fs-laser beam creates coherent exciton-polariton modes that interfere and form a dynamical grating which evolves in

time. Due to the lifetime of polaritons being extremely short (less than 1 ps), the exciton-polariton modes transform into self-trapped excitons that permanently freeze the polarization grating in the glass, thereby explaining the distribution of the nanograting and, in particular, the two distinct periodicities.

2.3.3 Microvoids

In 1997, spherically-shaped tiny voids confined to submicrometre domains were observed in fused silica after fs-laser irradiation at high pulse energies (>500 nJ). Several studies demonstrated that these structures consist of a hollow core surrounded by a densified shell of modified fused silica [4, 33, 99]. Additionally, they possess a spherical shape with a diameter around 200-250 nm. Further, index profile measurements demonstrated that the refractive index contrast between the void and its surroundings can be as high as 0.45, which roughly matches the refractive index contrast between fused silica and air.

The formation of microvoids is described by a quick build-up of the pressure within the focal volume, as a result of the high energy of the incident pulse, which causes the temperature to increase to 10^6K . This sudden increase generates a shockwave that propagates outward of the focal volume, and ejects the vaporized material into the surroundings, thereby explaining the denser phase observed around the microvoid [4, 99]. The pulse energies necessary to observe this modification also induce self-focusing, which further narrows the beam waist and justify the submicrometric size of the voids.

2.4 Conclusions

In this chapter, the fundamentals behind the interaction between a fs-laser beam and transparent media were reviewed. When focused inside the material, the ultrashort pulse duration and high peak intensities of the laser beam can trigger non-linear absorption and ionization processes, where the laser energy is transferred to electronic excitations. The subsequent relaxation of the free electrons through radiative or non-radiative recombination processes or through the formation of point defects mediated by self-trapped excitons, leads to a structural modification of the irradiated volume. The non-linear nature of the absorption process confines the laser-induced modification to the focal volume, whereas its composition and morphology depend on the exposure parameters and on the properties of the irradiated material. In comparison to conventional microfabrication technologies, fs-laser micromachining enables not only surface but also volume processing with submicrometric resolution. Further, pure three-dimensional devices can be made by patterning the movement of the sample in relation to the focus. Moreover, different kinds of systems can be integrated in either a planar or fiber geometry owing to the localized nature of the laser-induced modification.

Ultrafast laser inscription can also be applied to a wide range of materials, including glasses, crystals and polymers. In this thesis, though, the focus is on the fabrication of optofluidic devices in fused silica planar substrates. Accordingly, two main modifications

were explored, from which the devices presented in this research work can be fabricated. One of those consists in a local isotropic increase of the refractive index due to densification mediated by point defects, which enables the formation of optical waveguides with a refractive index contrast around $10^{-4} - 10^{-2}$, where light is guided through the irradiated path. A second material transformation is linked to the formation of nanogratings, which are composed by periodic planes of nanoporous material or nanocracks intermediated by modified silica. As will be explained in more detail in chapter 4, these structures are etched, in either HF acid or in KOH, at a much higher rate the pristine medium, which facilitates the construction of microfluidic channels.

Chapter 3

Experimental Methods

In this chapter, the fabrication and characterization techniques used to form and study the optofluidic devices presented in this thesis are discussed. First, section 3.1 provides a description of the fs-laser system and of the laser direct writing unit used to design and write the optofluidic devices, alongside the protocol for alignment of the experimental setup. This is accompanied by the procedures for chemical etching, in either HF acid or KOH, and for thermal annealing, which are associated to the formation of microfluidic channels. The protocols for sample preparation and cleaning, and for polishing are also established. Lastly, section 3.2 details the characterization setups for measuring the insertion losses of the optical waveguides, together with the optical and SEM microscopy and the contact profilometry systems used to study the morphology and topography of the fabricated devices.

3.1 Experimental Methods

3.1.1 Femtosecond Laser System and Laser Direct Writing Workstation

Laser direct writing is carried on a femtoLAB workstation (Workshop of Photonics) that features several components for adjusting the power and polarization of the fs-laser beam and for focusing the beam inside the substrate. It also includes a software interface (SCA) that controls all hardware units and where the movement of the linear translation stages and/or the galvoscaner is programmed to fabricate three-dimensional devices in a user-defined geometry¹.

The fs-laser system used is a fiber-amplified diode-pumped Amplitude Systèmes Satsuma HP laser, which generates 250 fs-long pulses (at a repetition rate of 500 kHz) with a Gaussian mode profile (TEM_{00}). The fs-laser pulse has a beam size of $2.35 \times 2.20 \text{ mm}^2$ and $M^2(X, Y)$ of $(1.11, 1.14) - (1.11, 1.13)$ at a fundamental wavelength

¹Initial tests, and in particular those reported in annex B, were conducted with a different laser direct writing unit. Details regarding this system and its alignment can be found in [119]. Although the experimental setup is assembled in a similar fashion to the one described in this section, the components (linear translation stages, focusing lens, beam expander) are different. In particular, in the system previously held in place, a New Focus 5722 A-H aspheric lens with a numerical aperture of 0.55 and a 2.9 mm working distance was used.

of 1030 nm. The system can operate on a single-shot exposure regime or it can provide a train of fs-laser pulses with controllable repetition rate ranging from 0.5 MHz to 40 MHz. It also features a harmonic generation module capable of converting the fundamental beam to either its second (515 nm) or third (343 nm) harmonics. Throughout this dissertation, laser direct writing is always performed at 515 nm as it provides a higher spatial confinement than irradiation at 343 nm due to the higher number of photons involved in the ionization process, and a higher photoionization rate (for exposure in fused silica) than the 1030 nm beam [87, 101]. The maximum pulse energy of the second harmonic beam is 11 μJ , and can be controlled internally through an acousto-optic modulator; during this work, the modulator efficiency is kept at 50%. The laser output is triggered externally by the SCA software, upon execution of the design algorithm.

Although the workstation is equipped with optical components for beam delivery at all three laser wavelengths, here only the optical path of the 515 nm beam is described. The experimental setup is shown in figure 3.1. The workstation is mounted on a granite base which ensures mechanical stability during laser direct writing, and is kept inside a Class 1 safety enclosure which besides providing a safer environment for laser direct writing also isolates the system from mechanical vibrations and prevents the optical components from environmental dust.

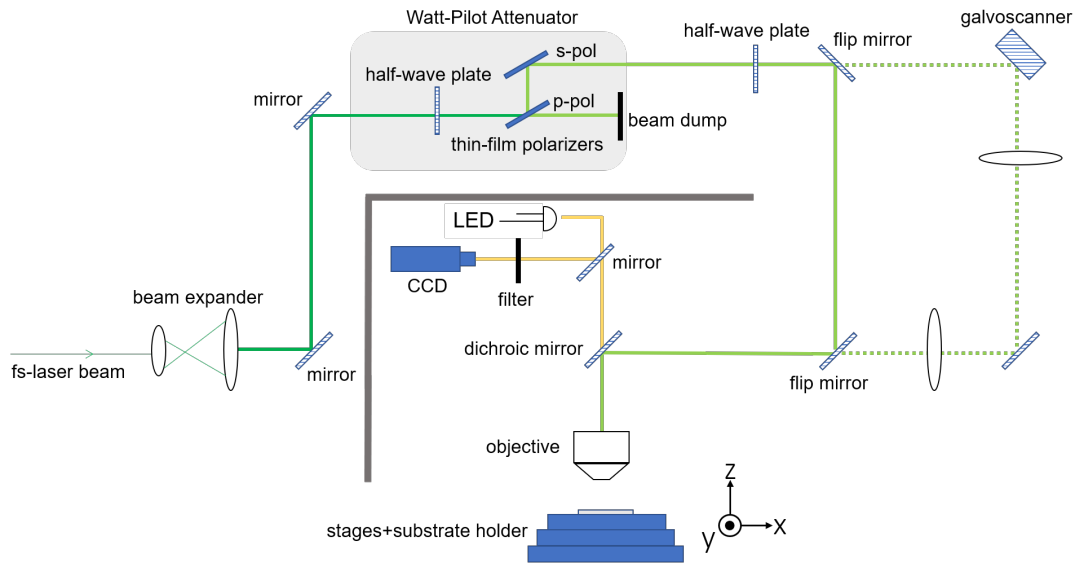


Figure 3.1: Experimental setup for fs-laser direct writing at 515 nm.

First, the fs-laser beam is driven through a beam expander that broadens the beam diameter to 2.5 mm and collimates it. This corrects the beam divergence associated to the fs-laser system, and decreases the intensity of the laser beam thereby minimizing the chances of damaging the optical components. The fs-laser beam is then directed to the power controlling unit by two mirrors set at 45° from the beam propagation direction. Dielectric mirrors, with a high reflectivity over 99% at 515 nm for 45° incidence, are used throughout the experimental setup for beam delivery. They are fitted in standard kinematic mounts and show no dispersion and a wavefront distortion of $\lambda/8$.

The power controlling unit consists of a motorized attenuator (Altechna Watt Pilot) assembled in the configuration shown in figure 3.1. This component is formed by a half-wave plate set transversal to the propagation direction of the fs-laser beam, which separates the incident beam into an s-polarized and a p-polarized beam. The intensity ratio of these two beams can be tuned by rotating the waveplate. Two Brewster type thin film polarizers are placed after the half-wave plate to spatially separate both polarizations. The s-polarized beam, because it has a higher polarization contrast, transverses towards the polarization controlling unit, whereas the p-polarized beam is guided towards a beam dump. This unit is externally controlled through the workstation's SCA software, which, in comparison to the laser system internal modulator, enables an easier definition of the pulse energy.

Control of the laser beam polarization is provided by a motorized half-wave plate, placed orthogonal to the direction of the propagation of the fs-laser beam. The waveplate is formed by crystalline quartz which is a birefringent medium that induces a π phase shift between the two polarized modes propagating along the fast and slow axis of the waveplate, respectively, thereby rotating the angle of polarization of the linearly polarized beam by 2α , where α is the angle between the initial polarization direction and the waveplate's fast axis. This component is also controlled by the workstation's SCA software, where the angle of rotation of the waveplate α can be defined at will. Although not used, s-waveplates made of UV-grade fused silica can also be introduced after the half-waveplate to convert the beam's polarization from linear to radial, azimuthal or spiral.

From there, a set of flip mirrors directs the laser beam into a dichroic mirror that reflects the 515 nm beam into the entrance of the objective focusing lens. The flip mirrors are again oriented at 45° from the incident direction. Although not used in this work, both flip mirrors can be removed at any instance in order to use a galvanometer scanner, which continuously deflects the fs-laser beam thereby enabling faster writing over the XY plane. To use the galvanometer, two lenses assembled in a 4f configuration are placed in-between the scanning head and the objective focusing lens. The galvoscaner provides a maximum scan angle of $\pm 20^\circ$ and can be used for either the 515 nm and 1030 nm fs-laser beam.

The writing lens is mounted on a platform that can be manually translated along the Z direction, and which contains micrometric-precision screws for centring the objective entrance along the XY plane in relation to the fs-laser beam and for correction of the platform's tilt angle. During this work, the laser beam is focused inside the substrate through a 0.42NA plan achromat objective (Mitutoyo M Plan Apo NIR 50 $\times$) with a focal length and working distance of 4 and 17 mm, respectively.

The substrate is held by vacuum on a sample holder made of stainless steel that is mounted on top of three Aerotech direct-drive translation stages responsible for moving the sample along the XY plane (ANT130XY-110 PLUS) and along the Z direction (ANT130V-5 PLUS). The XY stages have a travel range of 110 mm, accuracy of ± 300 nm and resolution of 1 nm, whereas the Z stage has a travel range of 5 mm, accuracy of ± 200 nm and resolution of 2 nm. The acceleration of the linear stages is

500 mm/s², and their movement is defined through the workstation's user interface.

Lastly, coaxial illumination reflected from the substrate's surface, or light from a LED source placed within the sample holder and refracted through the substrate, is transmitted through the dichroic mirror and focused into a CCD camera. This facilitates the alignment procedure and provides live imaging of the writing process.

Sample Preparation and System Alignment

Dust and other contaminants present at the substrate's surface can obstruct the path of the fs-laser beam, thereby preventing it to be focused within the substrate and leading to a decrease in the laser energy deposited in the material. Therefore, the sample has to be cleaned prior to laser direct writing. This is done by rinsing the substrate in successive solutions of acetone, ethanol and deionized water before drying it with a nitrogen spray gun. In more severe cases, the substrate can also be cleaned by submerging it for five to ten minutes in a piranha solution, formed by adding hydrogen peroxide to sulphuric acid until the temperature of the solution reaches 80°C.

Before placing the substrate over the sample holder, the laser direct writing unit also has to be aligned to ensure efficient beam delivery. First, in spite of being confined within a closed cage, all optical components are inspected to ensure that they are clean (special attention is devoted to the components prior to the power controlling unit as they are exposed to a laser beam of higher intensity and can damage more easily). If needed, the optical components are cleaned with a jet of compressed air, or with an optical wipe damped with ether. To verify the system's alignment, several manually adjustable apertures (irises) defining the correct beam path are placed in-between components. If the laser beam does not pass through the centre of one of these apertures, the optical component right before said aperture has to be realigned. After this verification, a mirror is placed over the sample holder and the position of the dichroic mirror is adjusted until the paths of the incident and reflected beam coincide; this assures that the sample holder is orthogonal to the direction of propagation of the laser beam. To guarantee that the fs-laser beam also travels parallel to the optical axis of the objective, a mirror is placed over the objective holder and the platform's tilt angle is adjusted until the incident and reflected paths coincide. Through this protocol, it is also assured that the sample and objective holders are parallel to each other.

From there, the objective is fastened to its holder and the quality of the focused beam is inspected by observing the irradiation pattern on a laser viewing card (placed far from the focus to facilitate inspection). If the pattern presents any scattering centres it means that the objective has to be cleaned (through a similar procedure to the other optical components), otherwise if it is clear the objective is in conditions to be used. Afterwards, the optical axis of the objective is centred relative to the laser beam. A laser viewing card is placed below the objective (far from its focus to facilitate the alignment) and the broadening of the irradiation pattern is observed by opening the iris placed immediately before the objective. If the pattern grows symmetrically it means that the objective is centred with the laser beam, otherwise the objective is displaced through actuation on

the micrometric screws until a symmetric pattern is observed. In addition, because the laser beam overfills the entrance aperture of the objective, the writing numerical aperture corresponds to the nominal values of the objective's numerical aperture. This also introduces significant losses in the system. Indeed, by measuring the laser power before and after the focusing lens, it was determined that 52.5% of the incident power is lost through the writing lens.



Figure 3.2: Ablation marks formed at the surface of fused silica.

Only after executing these steps, is the system considered aligned and is the substrate placed on its holder. Here, fused silica (Suprasil 1) substrates with $75 \times 25 \times 1 \text{ mm}^3$ with top and bottom surfaces polished to optical quality are used; the substrates can be cut to smaller dimensions with a dicing saw. With the substrate held by vacuum and with a low pulse energy, the Z-stage is translated until well-defined ablation marks, as illustrated in figure 3.2, are observed in the visualization window. Observation of these marks indicates that the laser beam is focused on the top surface of the substrate, and they can be used as reference for alignment. Afterwards, the command “Field Calibration” on the workstation’s SCA software is executed to centre the camera frame with the laser spot. Further, after determining the coordinates of the edges of the substrate through scanning the sample along the XY plane (while focused on the substrate’s surface), the substrate contour can be outlined in the visualization window through the command “Paint Line”. Both these processes superimpose the design on the visualization window and facilitate the definition of the writing coordinates. Then, given that the substrate may be uneven, the “Sample Tilt Detection” and “Transform” tools are performed to determine the pitch and roll angles within the writing region and to change the reference coordinate system, respectively, in order to assure that the laser beam is always focused at the desired depth. In most cases, the sample is uneven by less than 0.01° and this correction can be neglected. The “Transform” command can also be used to rotate the reference axis in order to correct for yaw caused by poorly placement of the substrate over the holder. This correction can be important, for instance, to assure that fs-laser written optical waveguides are orthogonal to the substrate’s facet as this will minimize optical coupling losses to a single-mode fiber due to geometrical misalignments.

With the substrate aligned, the laser beam polarisation and pulse energy are calibrated. Per definition, when initializing the system the polarisation angle is 0° which coincides with the Y direction (according to the coordinate system of figure 3.1). This angle is controlled through the command “Polarisation Rotator” which rotates the half-wave

plate, where an input of α rotates the polarisation angle clockwise by 2α . Similarly, the pulse energy is defined by the “Attenuator” command, where an input percentage rotates the halfwave plate on the Watt-Pilot unit, thereby changing the energy allocated to the s-polarised beam used for writing. Prior to laser direct writing, the pulse energy is measured and correlated through a linear fit to the “Attenuator” percentage. A photodiode (LaserPoint PD-50-D9-UV) or a thermal sensor (LaserPoint 10-BB-D25), with measurement ranges limited from 10 μ W to 50 mW and from 2 mW to 10 W respectively, connected to a LaserPoint PLUS2 sensor meter are used to measure the laser power after the focusing objective. The pulse energy (E_p) is then obtained indirectly through the relation $E_p = P/R$, where P is the measured laser power and R the repetition rate. As an aside, the fs-laser system should be turned on 1 to 2 hours before starting the writing procedure, in order for the pulse energy to stabilize. Throughout this dissertation, anytime the pulse energy is indicated it corresponds to the energy after the focusing objective.

After performing these alignment procedures, the algorithm programmed in the SCA interface is executed which will imprint the design of the device in the substrate at the user-defined coordinates.

Two possible writing approaches are typically used, which are illustrated in figure 3.3. In the longitudinal configuration, figure 3.3(a), the sample is translated parallel to the direction of propagation of the fs-laser beam, whereas in the transversal configuration, figure 3.3(b), the substrate is scanned orthogonally to this direction. Both writing approaches condition the size and shape of the irradiated laser-exposure track. The longitudinal configuration leads to laser-exposure tracks with circular cross-section, but with length usually limited by the working distance of the focusing lens. Meanwhile, centimetre-long tracks can be obtained through the transverse configuration, where the maximum length is defined by the working range of the translation stages. However, the resulting cross-section is generally elliptical with the major axis aligned with the direction of propagation of the fs-laser beam. As was discussed in section 2.2.4, this asymmetry is caused by the different beam waist radius (ω_0) and Rayleigh range (z_0). Consequently, this results in a ratio between the width and height of the laser-exposure track of $\frac{NA}{n}$, where NA is the numerical aperture and n is the refractive index of fused silica at the laser wavelength.

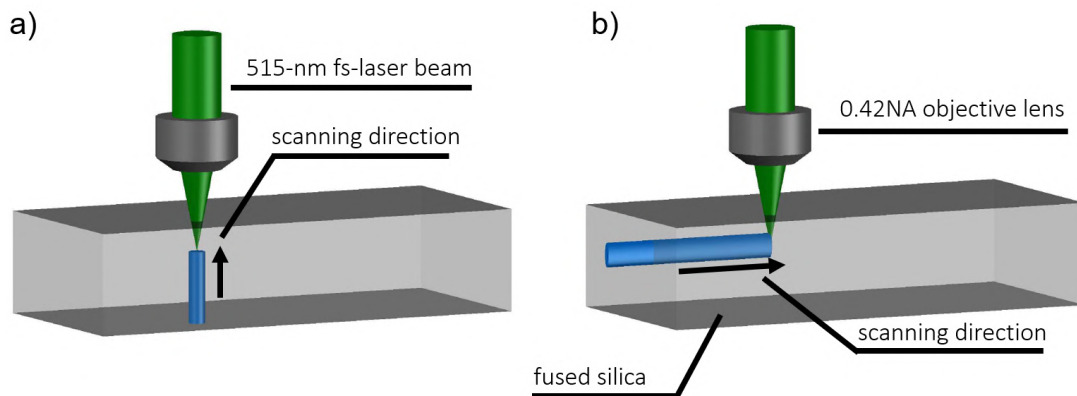


Figure 3.3: Writing configurations for (a) longitudinal and (b) transversal scanning.

Here, the devices were written through the transversal configuration. Accordingly, with the 0.42NA focusing lens used in this work, it is estimated that the height of the laser-induced modification is around 3.8 times larger than its width. Although not tested, symmetrical cross-sections could be obtained by using a higher numerical aperture lens [86], or by working at higher repetition rates (above 1 MHz) where thermal effects come into play [97]. Alternatively, beam shaping techniques involving the placement of a slit prior to the focusing lens [7, 8] could be used.

The writing technique of optical waveguides and microfluidic channels is based on the general configuration depicted in figure 3.4. Straight optical waveguides are written transversely by scanning the sample in the XY plane along the laser focus. Here, to prevent the “Quill” effect the laser-exposure tracks are always written by translating the sample in the positive X direction. Bended waveguides can also be fabricated, where the system synchronously moves both axes. In general, the algorithm is programmed manually by defining, in the SCA software, the polarisation of the laser beam, the pulse energy and the scanning range and speed of the translation(s) stage(s). Further, acceleration and deceleration margins are given in order to switch on or off the laser only when the scanning stage reaches the programmed velocity. This way, any issues related to over-writing at the start or end of the waveguide are avoided.

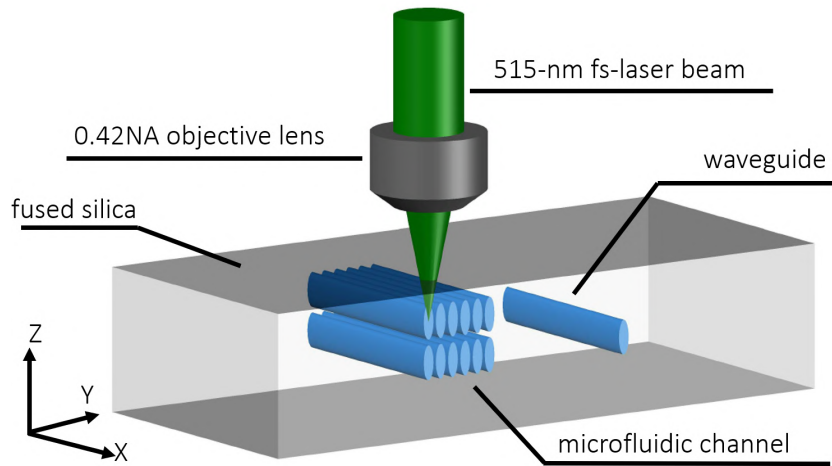


Figure 3.4: General writing configuration for optical waveguides and microfluidic channels.

Microfluidic channels are fabricated by stacking several laser-exposure tracks along X (or Y) and Z with a user-defined spacing between tracks. The algorithm can be either programmed manually by defining the position and length of each individual track, or by feeding the SCA software with a ‘.dxf’ file containing the design of the device which is then hatched and sliced according to the user criteria. Both options have their merits, with manual programming providing a finer control over the writing properties (pulse energy, scanning speed, laser beam polarisation) of the individual tracks, whereas for hollow microfluidic channels, hatching and slicing of the pre-designed device is easier to be implemented. In all cases, in-between scans a time delay of 500 ms is set to assure that the linear stages are at halt before writing the following track. Similarly, to the

writing of optical waveguides, margins for acceleration and deceleration are also defined for each track. Additionally, the laser-exposure tracks are scanned from the bottom to the top of the surface to guarantee that the laser beam only propagates through pristine material. Otherwise, in a top-to-bottom regime, the laser beam after writing the superficial layers would scatter or be distorted when focusing beneath the sample's surface and write over an already irradiated volume, thereby inducing a modification different from the one desired [32].

Lastly, due to refraction at the air-glass interface, the focusing depth does not equal the translation along the stage Z from the substrate's surface inwards (z_0). Based on the Snell's law of refraction and given the objective's numerical aperture of 0.42, the real focusing depth is $z = z_0 \frac{n_{\text{silica}}}{n_{\text{air}}}$. Moreover, although the working distance of the objective enables the fabrication at any depth of the substrate, the devices are usually fabricated at depths no longer than 150 μm to minimize spherical aberrations. In addition, since the bandwidth of the fs-laser beam, measured at full-width half-maximum, is 8.4-9.5 nm, chromatic aberrations can be neglected.

3.1.2 Chemical Etching

Chemical etching is performed after fs-laser direct writing in order to selectively remove the laser-irradiated regions and, in turn, create the microfluidic channel. Here, this reaction can be performed with two etchants: acid or KOH. Due to the higher etch rate, the chemical reaction is shorter when etching with HF acid than with KOH, but more hazardous to human health.

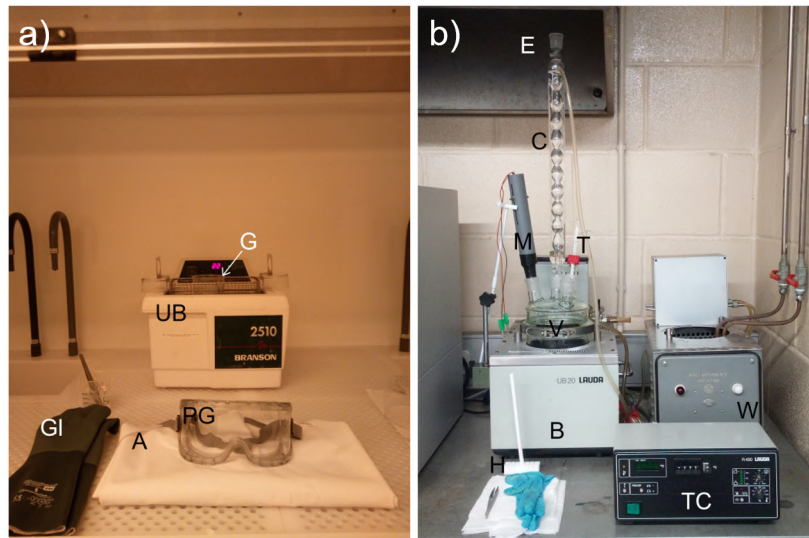


Figure 3.5: Experimental setups used for etching with (a) HF acid and (b) KOH. The setup for etching with HF acid includes the ultrasonics bath (UB), beaker with substrate (G), and protective material: gloves (GI), teflon apron (A) and glasses (PG). The setup for etching with KOH comprises the gas exhaustion system (E), Allihn condenser (C), temperature control unit (TC), water cooling unit (W) and bath (B), motorized blade (M), thermometer (T), reaction vessel (V) and substrate holder (H). Image was taken from [120].

Regardless of the chosen etchant, the substrate is always thoroughly cleaned and

inspected under an optical microscope prior to etching. During laser direct writing, the fs-laser beam, when focused near the sample's surface, can cause ablation with the removed debris accumulating at the surface. To prevent the debris from blocking the etchant from penetrating through the laser-modified volume, the sample is cleaned following the protocol described earlier. After cleaning, the laser-written regions are examined through optical microscopy to assure that their size and geometry match those of the design. The etching setups are shown in figure 3.5.

Hydrofluoric Acid

Being a hazardous species, handling of HF acid requires appropriate clothing (protective gloves, Teflon apron and safety goggles). Due to the same reasons, the entire procedure is done in an ISO-6/7 cleanroom facility.

The etching is performed in an ultrasonic bath (Branson 2510 Ultrasonics Cleaner) with a 10% volume concentration of HF acid diluted in deionized water. The ultrasonic cleaner generates sound waves with a 40 kHz frequency that causes the formation of bubbles and their subsequent implosion, which attack every surface and help remove the debris inside the microfluidic channel. Also, a volumetric concentration of 10% provides a high enough selectivity and a minimum etching time.

As cautioned by the manufacturer, the tank is filled with deionized water instead of the etching solution. Accordingly, the acid is first poured into a polyethylene beaker, and then placed inside a larger glass beaker which sits inside the ultrasonic tank. The ultrasonic cleaner increases the solution's temperature which affects the etching reaction, given that the etch rate is temperature-dependent. Therefore, before introducing the substrate within the etching solution, the ultrasounds machine is turned on until the temperature of the solution stabilizes at $30\pm5^{\circ}\text{C}$. Teflon tweezers are used to place the sample inside the beaker containing the HF acid. The sample is entirely immersed in the HF acid to prevent the formation of cracks at the substrate's surface.

After etching for a pre-determined period, the substrate is transferred into a beaker filled of deionized water that stops the etching reaction, and is then cleaned with a jet of compressed air. The sample can be further rinsed in an ultrasonic bath of ethanol followed by deionized water to remove any remnant debris. Then, the substrate is inspected under an optical microscopy to assess if the etching reaction is complete or if it should be extended.

Potassium Hydroxide

Besides being safer, KOH can also be used as an alternative to HF acid as it provides a higher etching selectivity, but at the expense of a lower etch rate that significantly slows down the etching reaction. Given that the etch rate is temperature dependent, a possible solution to reduce the duration of the etching reaction into a suitable time period is to perform it at higher temperatures (around $80\text{-}100^{\circ}\text{C}$).

Accordingly, the glass vessel containing an aqueous KOH solution with molar

concentration of 10 mol/dm^3 is placed in bain-marie that heats the etching solution to $85 \pm 1^\circ\text{C}$. The temperature of the solution is established by a LAUDA UB-20 ultra-thermostat with a LAUDA R400 electronic controller, and is continuously monitored during the etching reaction. In addition, a motorized three-bladed rotor stirs the solution to prevent the creation of temperature gradients within the bath, which may lead to a heterogeneous etching reaction. With this method, the temperature at all points inside the vessel is within 1°C of the target temperature.

The reactional vessel is closed by an Allihn condenser, which has cold water circulating inside it from bottom to top, while being pumped by a PM Tamson thermostatic bath and circulator. This way, KOH vapours produced due to the high temperature condense and return into the etching solution, thereby maintaining the concentration of the etching solution constant.

After the target temperature is reached, the sample is fixed on a homemade groove Teflon holder and immersed in the etching solution. Similar to etching with HF acid, the etching reaction is stopped by transferring the substrate into a deionized water bath and, following sample cleaning, the etching stage is evaluated by examining the sample through optical microscopy.

3.1.3 Thermal Annealing

When performed, thermal annealing is responsible for decreasing the average roughness of microstructures fabricated within the microfluidic channel, and for smoothing the channel's sidewalls and bottom surface. Prior to this process, the substrate is thoroughly cleaned to prevent any residual contaminant from interacting with the sample's surface and from altering its surface chemistry. Afterwards, the sample is placed over a ceramic base inside a Carbolite RHF 1500 furnace, which is then turned on. The adopted annealing protocol, for a target temperature of 1250°C , is illustrated in figure 3.6.

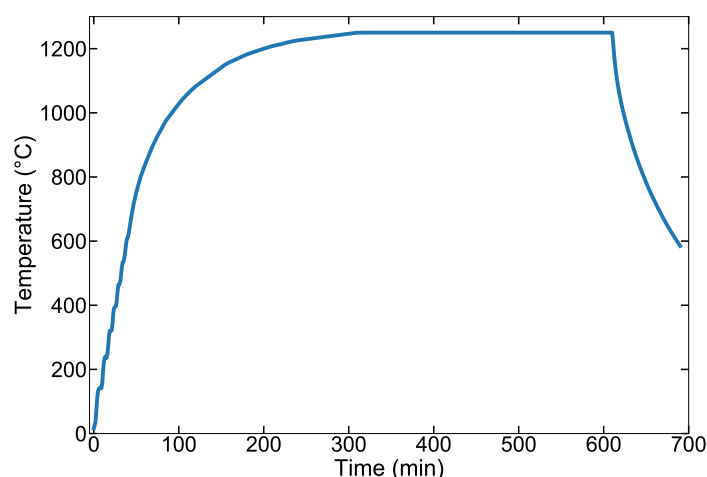


Figure 3.6: Heating and cooling curve for annealing at 1250°C .

The temperature of the furnace raises from room temperature ($20\text{--}25^\circ\text{C}$) to the setpoint (usually 1250°C), with an initial dwell rate of 15°C/min that decreases as the temperature

raises. For a target temperature of 1250°C, the system takes around five hours to reach this temperature as the heating rate progressively falls down to 0.1-0.2°C/min near 1250°C. After reaching the target temperature, a furnace-controlled feedback system keeps the substrate at this temperature in a dry atmosphere for an additional five hours. Upon completion of the annealing time, the system shuts down and the temperature furnace starts to decrease according to Fourier's law for thermal conduction. Cooling should be gradual to avoid the formation of permanent internal stresses that can cause either short-term or long-term failure. The sample is withdrawn from the furnace only after it cools down to room temperature. The entire process is conducted at atmospheric pressure without atmosphere control.

3.1.4 Polishing

The utilized fused silica substrates are bought with its edges frosted and seamed, as illustrated in figure 3.7(a). Consequently, this upsets any type of study of the cross-section of the laser-affected zone, while also increasing the optical losses when coupling light from an optical fiber into a fs-laser written waveguide. Additionally, even with polished edges, during laser direct writing the laser beam fails to converge to a single focal spot near the facets of the substrate due to refractive index mismatch in the air-glass interface [32]. This discontinuity causes a depletion of the laser power delivered to the focus, and a gradual disappearance or significant distortion of the modification near the end facets. In turn, this affects the fabrication of optical devices by increasing again the coupling losses [121], and of microfluidic channels by preventing the formation of nanogratings. For these reasons, the side facets of the substrate have to be ground polished. This process should be done after laser direct writing to circumvent the issues aforementioned, or after chemical etching if this procedure is performed and the etchant eliminates the waveguide's input/output section.

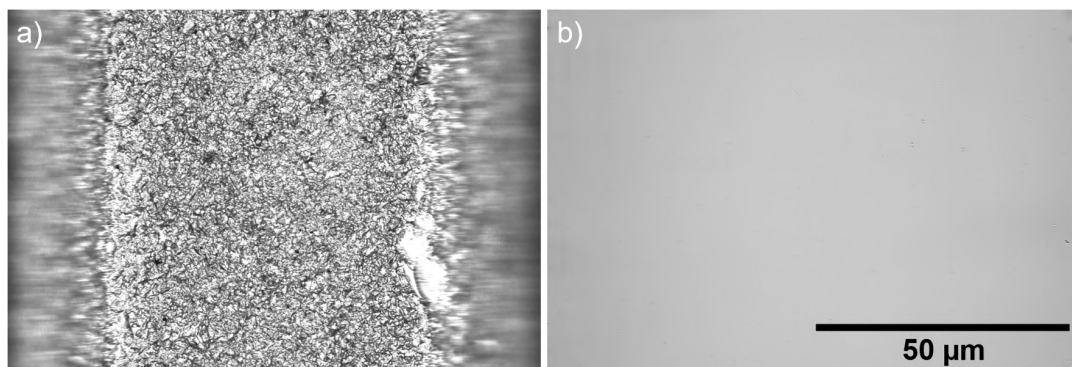


Figure 3.7: Microscope image of the substrate facets (a) before and (b) after mechanical polishing. The scaling bar is the same for both images.

Before polishing, the substrate has to be prepared according to figure 3.8. First, the substrate is bonded, with a temporary bonding wax Logitech 0CON-199, to a previously polished tempered glass that provides resistance to the whole assembly. The molten bonding wax is spread over the holding glass, after which the substrate is placed carefully

over the tempered glass to avoid the formation of bubbles. To minimize the polishing time, the borders of both glasses are aligned with each other by pressing the entire assembly against a thin glass slab. After the bonding wax re-solidifies, the alignment glasses are removed from the assembly, which is then mounted on the jig with the substrate's facet facing the polishing plate.

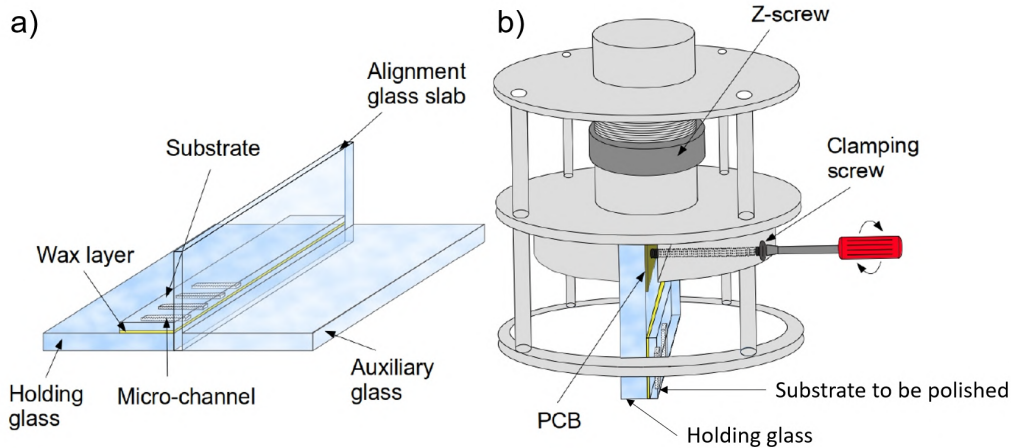


Figure 3.8: Illustration of the (a) assembly and alignment of the substrate with the holding glass and (b) of the placement of the glass within the jig.

Three different polishing suspensions are used, with successively smaller dimension of the suspended particles, which grind the substrate's facet until its surface becomes flat and with optical quality. The first polishing solution consists of a Logitech Silicon Carbide 600-grit powder dissolved in water, with an average particle size of $9\text{ }\mu\text{m}$, which continuously drips onto an iron polishing plate. With the jig placed over the polishing plate, both start to rotate at a low speed, while avoiding the substrate from touching the plate. To avoid chipping, the substrate is gently released and slowly put in contact with the plate. This stage is the most critical in the whole process, due to the risk of the substrate being released from the tempered glass and/or starting to fracture. When there is a large surface of the substrates in contact with the plate, this assembly can be entirely dropped. At that point, the plate rotation can also be increased to around 20 rpm, while having 2/3 drops of polishing fluid per rotation in order to keep the plate wet and to avoid abrasive polishing. To improve the surface quality and polishing uniformity, the jig rotates around its axis. The polishing is interrupted periodically to inspect, through optical microscopy, the surface of the polishing facet. If it is uniform and does not present any major scratches on its surface, the jig can be transferred to the next polishing machine. The second and third polishing solutions consist of Logitech Aluminium Oxide (with an average particle diameter of $5.1\text{ }\mu\text{m}$) and Logitech SF1 polishing fluids which drizzle over a grooved brass plate and an expanded polyurethane padded-plate, respectively. The procedure is repeated for each plate, with the jig and substrate being thoroughly cleaned with water in-between polishing steps to ensure that there is no cross-contamination. After polishing, the substrate is first separated from the tempered glass by melting the bonding wax, and is then cleaned (following the methods outlined earlier) to remove any remaining

debris. In the end, the facet should be transparent, uniform and crack-free as illustrated in figure 3.7(b).

3.2 Characterization Techniques

3.2.1 Optical and Scanning Electron Microscopy

Different microscopy techniques are used to study the morphology and topography of the laser-induced modifications and of the fabricated devices. In both cases, the samples are cleaned and dried to avoid any residual debris from interfering with the image quality.

Optical waveguides and microfluidic channels are always characterized after laser direct writing, chemical etching and/or thermal annealing through top view and cross-section images retrieved with an optical microscope (Leica DM 6000) with 200 $\times$ magnification.

The microstructures described in section 6 are also analysed through scanning electron microscopy (SEM). The images are obtained with a high resolution (Schottky) Environmental Scanning Electron Microscope with X-ray Microanalysis and Electron Backscattered Diffraction analysis (FEI Quanta 400 FEG SEM / EDAX Genesis X4M) from the Materials Centre of the University of Porto (CEMUP). Image formation is attributed to the detection of secondary electrons emitted from the substrate's surface after interaction with the incident electron beam. Due to fused silica being a non-conductive material, the substrates have to be first coated with an Au/Pd film by sputtering (SPI module Sputter Coater equipment) to prevent charge accumulation in the substrate's surface which otherwise affects the image quality. For the same reason, the microscope is operated in a low vacuum environment.

3.2.2 Contact Profilometry

In section 6, the surface profile and surface roughness of the microfluidic channel are also characterized, after chemical etching and thermal annealing, through contact profilometry with a Dektak XT Bruker profilometer. First, the substrate is cleaned to assure that no debris or contaminants are inside the microfluidic channel, as they can affect the measurement. The sample is then placed over a standard holder that is mounted on top of two linear translation stages. These stages move the sample across the profile stylus, who is in contact with the sample's surface and whose height varies during scanning in order to keep the exerted force constant. The measurement resolution is 0.035 $\mu\text{m}/\text{point}$, with a profile tip terminating in a 45° cone and with a tip radius of 2.5 μm being used. To characterize the surface profile of the microfluidic channel, the scanning direction is defined to be orthogonal to the direction the laser-exposure tracks are written with. The dimensions of the microfluidic channel are scaled to enable perfect contact of the profile stylus with its surface, and to avoid scanning near the channel's sidewalls where the measurement error is higher. Additionally, the measurement setup is mechanically isolated from other lab equipment to remove possible noise sources.

3.2.3 Optical Characterization

The optofluidic devices reported throughout this thesis are characterized by measuring the insertion losses through the basic setup shown in figure 3.9.

Before any measurement, the device is cleaned following the procedure outlined earlier. In particular, the substrate facets containing the terminations of the optical waveguides and the microfluidic channels (when intercepted by an optical waveguide) have to be cleaned to assure the inexistence of contaminants, which otherwise increase the coupling and scattering losses, respectively. The optical fiber connectors of the light source, the optical detector or any other external device are also cleaned with an optical fiber pen cleaner, whereas the optical fiber connectors are cleaned with dry wipes and inspected with an optical fiber microscope (FAVA FOM-400). These procedures are performed to assure that there are no coupling losses in-between interfaces.

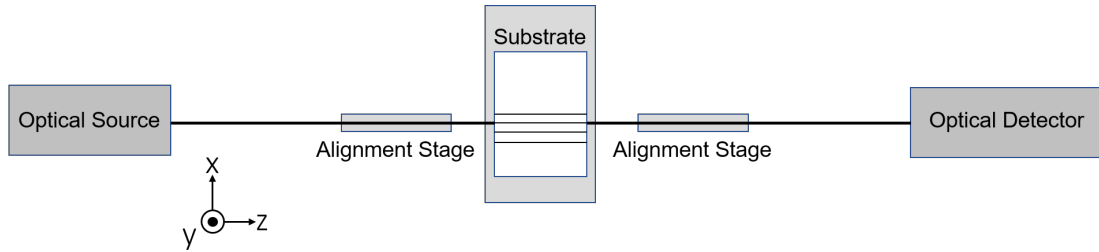


Figure 3.9: Setup for measurement of the insertion loss of optical waveguides.

As illustrated in figure 3.9, an optical source is connected into a single-mode fiber SMF28 with APC termination to avoid back-reflections (OPNETI), while its free-end is cleaved and butt-coupled to the entrance of the fs-laser written waveguide. Light coming out of the waveguide is similarly coupled into another optical fiber and collected by an optical detector. The input/output optical fibers are aligned with the entrance and exit of the fs-laser written optical waveguides, respectively, in order to maximize the coupling efficiency. To do so, the cleaved end of the two single-mode fibers SMF28 (OPNETI) rests over a grooved plate that is mounted on Elliot Martock MDE881 precision stages with three degrees of freedom (X, Y and Z) each connected to a piezoelectric adjuster (Dali E-2100) for nanometric resolution. Meanwhile, the substrate is placed over a precision stage with four degrees of freedom (X, Z, yaw and pitch) to complement the alignment, and is kept stable during measurements. Index matching (Cargille series AA $n_D^{25^\circ\text{C}} = 1.4580 \pm 0.0002$) is also used at the input/output facet to minimize Fresnel reflections due to the refractive-index mismatched interfaces and, in turn, improve optical coupling.

Different optical sources and detectors were used throughout this dissertation, and are detailed in the respective chapters. In all cases, the optical source is switched on well before any measurement, in order for it to stabilize and to prevent any variations in the optical power during the characterization. Further, the gathered spectra are always normalized to the optical spectrum of the radiation source.

Further alterations can be implemented in the measurement setup, depending on the

object of study. In section 5, to measure light reflected from a Fabry-Pérot cavity fabricated within a fused silica substrate, the radiation source is connected to a three-port optical circulator as shown in figure 3.10. Light emitted from the source is transmitted through one of the ports to the coupling optical fiber (which is butt-coupled to the entrance of the fs-laser written waveguide), while light reflected from this fiber exits the circulator from another port and is connected through another SMF28 optical fiber to the optical detector.

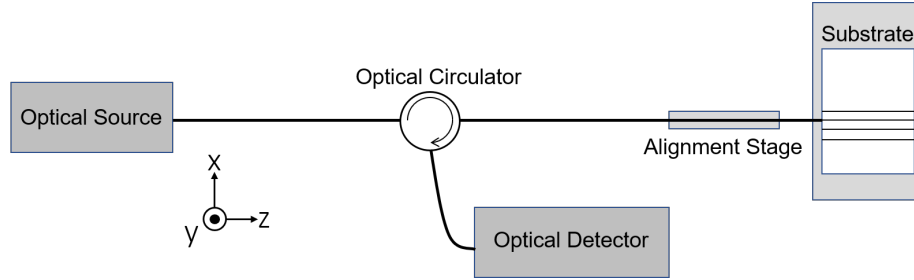


Figure 3.10: Setup for measurement of the reflected spectrum.

The optical sources used emit either unpolarized light or light linearly polarized along an unknown direction. In section 6, to characterize the WGM resonances of a microdisk it is more advantageous to measure the insertion losses with known polarization as this enables excitation of pure TE or TM modes. Therefore, the setup of figure 3.11 is used instead, where the optical source is now connected to an in-line fiber polarizer (ThorLabs ILP1550 PM-APC) followed by a PM fiber (Fujikura PM1550) whose free-end is butt-coupled to the lead-in waveguide. The former fiber allows propagation of light in one polarization while blocking the orthogonal polarization, whereas the latter maintains the linear polarization of the optical mode throughout its entire length. The free-end of the polarization maintaining fiber is mounted on an Elliot Martock fiber rotator stage that controls the input polarization angle with an uncertainty of $\pm 5^\circ$.

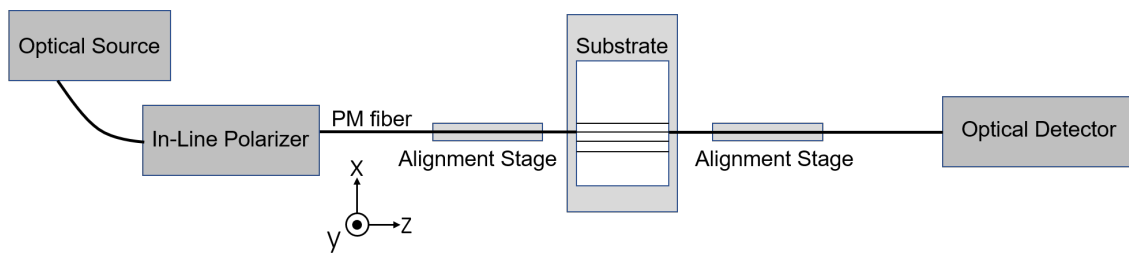


Figure 3.11: Setup for measurement of the insertion loss with polarization control.

Chapter 4

Microfluidic Channels: Calibration of Writing and Etching Parameters

In this chapter, it is discussed the fabrication of microfluidic channels in fused silica through femtosecond laser direct writing followed by chemical etching. Here, the microfluidic channels are designed by stacking multiple laser-exposure tracks along the horizontal and/or vertical directions with a uniform spacing between each, with all tracks being written with equal pulse energy and translation velocity. The influence of the laser direct writing parameters and of the etching agent on the etching dynamics is evaluated through measurement of the longitudinal and vertical etch rates and through analysis of the cross-sectional profile. The effect of the scanning density on the appearance of cracks and on the surface roughness is also considered. Based on this study, the optimal exposure parameters and etching conditions that enable the fabrication of rectangular-shaped microfluidic channels with uniform aspect ratio throughout its length and with low surface roughness are determined.

4.1 Introduction

As discussed in chapter 2, fs-laser irradiation can be used not only to form passive or active optical devices, but also to fabricate microfluidic channels when following laser direct writing by chemical etching. In fact, the first demonstration of microfluidic channels made in fused silica by this technique came in 2001 by Marcinkevicius *et al* [31] and, since then, several articles highlighting its potential in the construction of microfluidic and optofluidic devices have been published [41].

The formation of microfluidic channels in fused silica relies on the generation of etching selectivity, where the laser-modified volume is etched at a faster rate than the pristine medium. Although an increase in etch rate also occurs if the laser-induced modification manifests itself as an isotropic increase of the refractive index, an etching selectivity two orders of magnitude higher is obtained when working in a regime where the laser-modified volume is composed by nanogratings [36]. Still, given the difficulties in understanding the exact morphology of the nanogratings, the underlying mechanisms

responsible for the enhanced etching selectivity remain unclear. Hnatovsky *et al* [32], for instance, considered the nanogratings to be formed by an array of nanocracks periodically assembled along the polarization of the fs-laser beam, assuming a linearly polarized incident beam, through which the etchant can penetrate and dissolve the intermediate layers. On the other hand, recent reports suggest that the nanogratings are in fact composed by nanoporous layers of decomposed silica set in-between layers of weakly modified silica, which point to an alternate etching mechanism [116]. According to this interpretation, Bellouard's group have suggested that the etching selectivity is a result of localized densification coupled to stress accumulation and relaxation [117, 118]. In particular, the incident fs-laser beam leads to the gradual formation of a self-organized nanoporous structure with stress building up within the material. Experimental studies have revealed the existence of compressive stressed zones surrounding the nanopores which is linked to a decrease in the Si–O–Si bond angle, while analysis of the Raman spectrum has pointed to the formation of 3-membered ring structures within these regions which indicates densification of the glass matrix. Both of these modifications are more susceptible to etching. The decrease of the bridging angle increases the reactivity of oxygen due to the deformed configuration of the oxygen's valence electrons [31], while the strained Si–O–Si bonds are more vulnerable to attack than the stable six-membered ring structure defining the pristine medium [38]. The nanopores themselves, which comprise of silica-rich structures and oxygen-deficient centres, may also etch faster than the pristine medium [38]. Further, this model also implies that, above a critical amount of deposited energy, cracks start to nucleate randomly and to propagate through the laser-affected zone which is accompanied by relaxation of stress in the area surrounding the irradiated volume. Although these cracks may offer a path for the etchant to penetrate inside the material, their presence is thought to be counter-productive with the etching mechanism being much less efficient than the densification-driven and stress-induced one.

Regardless if the nanogratings are formed of parallel nanocracks or porous silica, the general consensus is that these structures are responsible for the increase in etching selectivity of the laser-irradiated volume. At the same time, both models are compatible with the experimental observations that the etch rate (and therefore the etching selectivity) strongly depends on the polarization of the fs-laser beam. As shown in figure 4.1(a), the etch rate along a single laser-exposure track is minimum if the polarization direction of the incident linearly polarized fs-laser beam is parallel to the scanning direction (angles of 0° and 180°), while it quickly grows and reaches a maximum when both directions become orthogonal to each other (90°). The source of this polarization anisotropy is understood by considering the formation of the nanogratings [32, 33]. If the polarization of the fs-laser beam is parallel to the scanning direction, the nanogratings align perpendicularly along the translation direction as depicted in figure 4.1(b). Accordingly, the etchant encounters alternate layers of nanocracks/densified zones responsible for the etching selectivity in-between layers of material that etches slowly, which reduce the cumulative etch rate. Meantime, if the laser polarization is orthogonal to the scanning direction, the nanogratings become longitudinally aligned, as illustrated in figure 4.1(c), which provides

a higher etch rate since the etchant flow is virtually unobstructed. The results shown in figure 4.1(a) reveal a selectivity of around 10:1 between the maximum and minimum etch rate. Still, this ratio is known to decrease as the pulse energy grows due to the periodic nanograting planes being replaced by a disruptive modification that shows no preferential alignment [36].

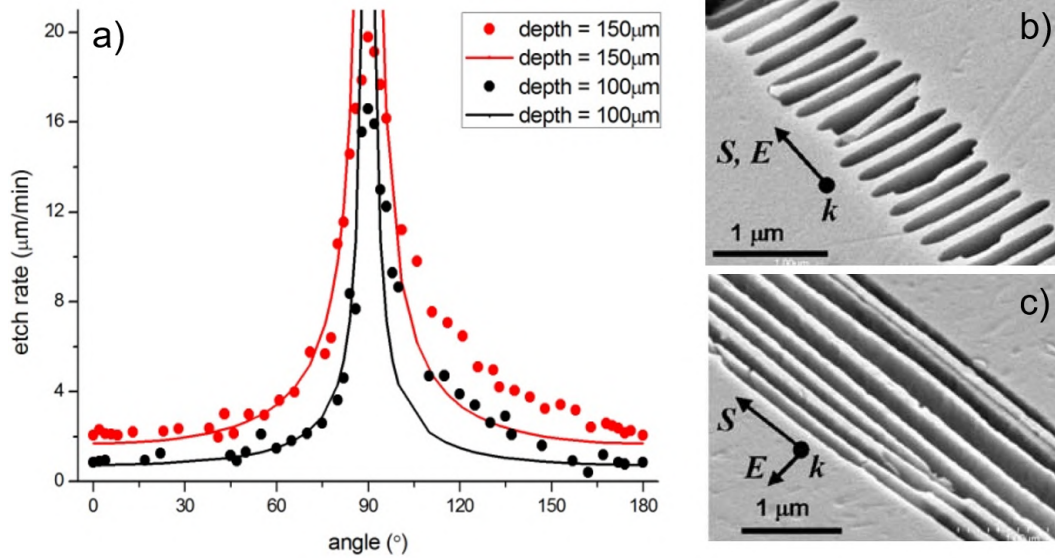


Figure 4.1: (a) Etch rate against the polarization angle of the incident linearly polarized fs-laser beam, and top view SEM images of the nanogratings revealing their alignment when the laser beam is polarized (b) parallel (0° and 180°) and (c) perpendicular (90°) to the scanning direction. The vectors S , E and k correspond to the scanning direction, to the polarization direction of the fs-laser beam and to the direction of propagation of the incident beam, respectively. Image (a) was taken from [119], while images (b) and (c) were taken from [32] where the laser-irradiated volume was weakly etched in HF acid prior to imaging.

Although perfect alignment of the nanogratings, and consequently of the polarization direction of the fs-laser beam, is necessary to maximize the etching selectivity, this parameter is not the only one to affect the selectivity. As detailed in chapter 2, the formation of nanogratings only occurs in a narrow processing window. Three different material transformations may arise in fused silica, with nanogratings being observed only within a limited energy range. Further, in the case of fused silica, writing at repetition rates higher than 1 MHz may trigger heat-accumulation effects that prevent the formation of these structures [105, 112]. Meantime, the build-up of nanogratings is also known to be dependent on the number of incident pulses [105], which are linked to the relation between the laser repetition rate and translation velocity. The duration of the laser direct writing process is also determined by these two latter parameters. The focusing conditions also affect the cross-sectional shape of the laser-irradiated volume and, in turn, the profile of the microfluidic channel. Additionally, spherical aberrations caused by the air-silica mismatched interface can distort the focal volume and decrease the peak intensity, leading to a higher pulse energy threshold for the formation of nanogratings and to a lower etching selectivity when focusing the fs-laser beam at greater depths [122].

Spatial recombination of fs-laser pulses can also alter the etching dynamics [123].

Meanwhile, the etching selectivity is also dependent on the used etching agent. Though HF acid and KOH are typically used as etchants, given that the Si–O–Si bond is more easily broken by the attack of F^- and OH^- , respectively, the reactivity of each species is influenced by the concentration and temperature of the solution. Moreover, etching with buffered HF solutions can also affect the etch rate and/or the morphology of the etched volume. For example, mixing with HNO_3 increases the etch rate due to the strong oxidability of the buffer etchant which facilitates the reaction between HF acid and the glass, while mixing with H_3PO_4 leads to a lower etch rate. Lower surface roughness can also be obtained by using buffered HF solutions mixed with NH_4F , H_2SO_4 or HCl .

In all, not only is the etching selectivity dose-dependent, but the duration of the fabrication process and the morphology and surface profile of the etched volume depend on the writing and etching conditions as well. Further, due to the importance microfluidic channels assume in the context of the optofluidic devices reported in the following chapters, it is then necessary to calibrate its fabrication procedure. Accordingly, the goals of this chapter are to study how the writing and etching parameters affect the etching dynamics and to determine the ideal conditions that enable the fabrication of rectangular-shaped microfluidic channels with uniform aspect ratio along its length and with smooth inner walls, while also minimizing the fabrication time. Given that the etching selectivity depends on multiple parameters, some considerations are made *a priori*. First, the laser repetition rate is fixed at 500 kHz in order to avoid operation in heat accumulation regimes, which narrow down the processing window for formation of nanogratings. For reference, the thermal diffusion time for fused silica is 1 μs , which determines the onset for these effects to be around a laser repetition rate of 1 MHz. Second, solutions of HF acid in a volumetric concentration of 10% and of KOH in a molar concentration of 10 mol/dm³ are used as etchants, as these are commonly used in the literature and offer a suitable trade-off between speed and control during the etching reaction.

Additionally, the microfluidic channels are also written following a transversal configuration where the substrate is scanned across to the laser focus, as shown in figure 4.2. Channels can be realized either by writing a single laser-exposure track or by assembling them along a one- or two-dimensional array with each individual track being periodically spaced from one another by a gap dy and/or dz along the horizontal and/or vertical direction(s), respectively. In particular, the latter approach enables the formation of wider three-dimensional microfluidic channels with complex geometry and variable size. Further, these are also written following a bottom-to-top approach to prevent over-writing effects and distortion of the laser focus by the modified regions upstream of the laser beam, which reduces the etch rate [32].

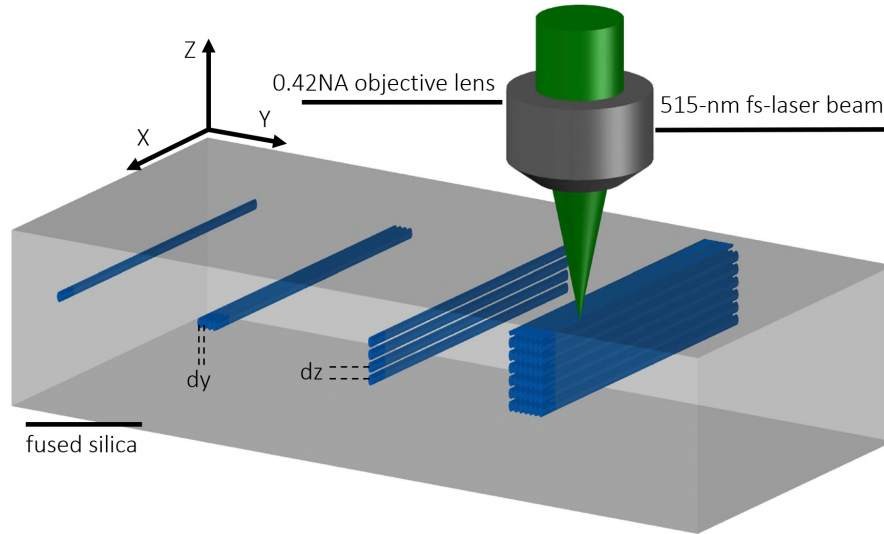


Figure 4.2: Writing configuration of the microfluidic channels.

The chapter is organized as follows. Following this introduction, the influence of the pulse energy and translation velocity on the longitudinal etch rate of single laser-exposure tracks is determined, and the effect of the etchant on the etching selectivity is discussed. This is complemented by analysing the cross-sectional profile against the writing parameters and its evolution during the chemical etching reaction. Then, etching of microfluidic channels formed by assembling multiple laser-exposure tracks is analysed. Besides the effect on longitudinal and vertical etch rate, it is also evaluated how the pulse energy, translation velocity and scanning density contribute to the formation of crack-free microfluidic channels with low surface roughness. It is also examined how the duration of the laser direct writing process can be shortened by adjusting the scanning density and translation velocity. Lastly, although a similar work had been conducted during the MSc thesis [119], the change in the laser direct writing workstation warranted a re-calibration of the fabrication parameters. In addition, this was also used as an opportunity to expand the processing window and to study the influence of other parameters.

4.2 Etching of Single-Scan Laser-Exposure Tracks

To understand how the etch rate, etching selectivity and cross-section profile of the laser-modified volume are affected by the inscription parameters for fs-laser direct writing, namely pulse energy and translation velocity, and by the chemical agent used for etching, in particular HF acid and KOH, two similarly-designed devices were fabricated and etched in the respective solution. Each device contained multiple 1-cm long single-scan laser-exposure tracks written 100 μm beneath the surface of the substrate at specific energy doses, with the laser repetition rate fixed at 500 kHz and with the fs-laser beam polarized orthogonally to the scanning direction. The pulse energy and translation velocity spanned from 25 nJ to 150 nJ and from 100 $\mu\text{m/s}$ to 5000 $\mu\text{m/s}$, respectively. All laser-exposure tracks were written along the +X direction according to the design proposed in figure 4.2. After laser direct writing, the facets of the substrate

were mechanically polished to remove the tapered region created by the refractive index mismatch when focusing the fs-laser beam on the edge of the substrate, and to enable visual inspection of the cross-section of the laser-induced modification under an optical microscope.

Each device was then etched in its respective solution: HF acid in a 10% volumetric concentration at $30\pm5^\circ\text{C}$ and KOH in a molar concentration of 10 mol/dm^3 at $85\pm1^\circ\text{C}$ (see section 3.1.2). The cumulative etching time was 60 minutes when etching with HF acid and 360 minutes when etching with KOH. In both cases, the etching was done non-consecutively for both reactions, being stopped after a certain time interval to inspect the profile of the laser-irradiated volume, through top view and cross-section imaging under an optical microscope. In particular, the cumulative etched length after each etching period was measured from the top view images, from which the etch rate of the single-scan laser exposure tracks was estimated. By modelling the gathered data with a linear regression, the computed slope equals the etch rate of the single-scan laser-exposure tracks (R_{wvg}) minus the etch rate of the pristine material (R_{silica}), which amounts to $0.097\pm0.005\text{ }\mu\text{m/min}$ when etching with the HF acid solution and $0.0020\pm0.0002\text{ }\mu\text{m/min}$ when etching with KOH. Further, similarly to the measurement procedure outlined in [32], only the data pertaining to a cumulative etched length lower than $200\text{ }\mu\text{m}$ was considered for this calculation, given that after it the etched length started to decrease due to a saturation effect caused by the inability of the etchant to reach the laser-induced modification. In addition, some top view images of the volume etched in KOH revealed random interruptions which correspond to the precipitation of etched products, namely $\text{Si}(\text{OH})_4$, within the microfluidic channel [38]. These precipitates were removed in-between etching stages by cleaning the substrate in an ultrasonic bath of deionized water. Precipitation of residual products was not observed in the substrate etched in HF acid.

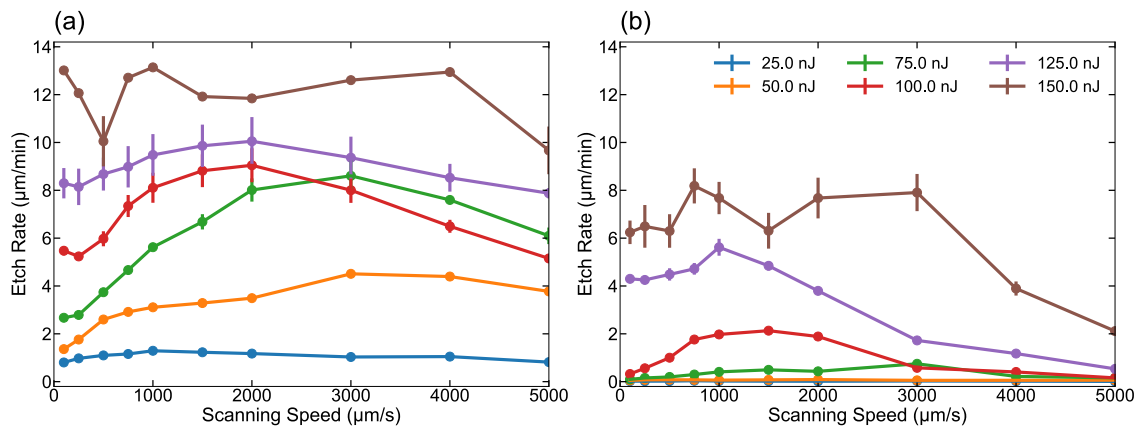


Figure 4.3: Etch rate of single-scan laser-exposure tracks against pulse energy and translation velocity for etching with (a) HF acid and (b) KOH.

The computed etch rate of the single-scan laser exposure tracks is shown in figure 4.3, for both etchants and against the tested irradiation parameters. A similar behaviour is

obtained when etching with HF acid or KOH, as expected and as confirmed in [122] as well. The etch rate generally increased with the pulse energy for a given translation velocity, and grew with the scanning speed until reaching an energy-dependent maximum before reducing again as the velocity kept increasing. In particular, with HF acid as etchant, the etch rate is around 1.00 ± 0.02 $\mu\text{m}/\text{min}$ for a pulse energy of 25 nJ regardless of the scanning speed. With a pulse energy of 50 nJ and 75 nJ, the etch rate increases with the scanning speed from 100 $\mu\text{m}/\text{s}$ to 3000 $\mu\text{m}/\text{s}$, reaching a maximum of 4.51 ± 0.12 $\mu\text{m}/\text{min}$ and 8.61 ± 0.64 $\mu\text{m}/\text{min}$, respectively, and decreases with the translation velocity above 3000 $\mu\text{m}/\text{s}$. An identical trend is observed when writing with a pulse energy of 100 nJ and 125 nJ, with the difference that a maximum etch rate of 9.04 ± 0.71 $\mu\text{m}/\text{min}$ and 10.05 ± 1.01 $\mu\text{m}/\text{min}$, respectively, is now obtained at 2000 $\mu\text{m}/\text{s}$ rather than at 3000 $\mu\text{m}/\text{s}$. With a pulse energy of 150 nJ, the etch rate is around 12.50 ± 1.00 $\mu\text{m}/\text{min}$ for scanning speeds lower than 4000 $\mu\text{m}/\text{s}$ and decreases from there on. Analysing the results obtained when etching with KOH, an insignificant etch rate of 0.020 ± 0.001 $\mu\text{m}/\text{min}$ and 0.070 ± 0.001 $\mu\text{m}/\text{min}$ is obtained for a respective pulse energy of 25 nJ and 50 nJ regardless of the translation velocity. For pulse energies of 75 nJ, 100 nJ and 125 nJ, the etch rate increases with the scanning speed until reaching a maximum of 0.75 ± 0.03 $\mu\text{m}/\text{min}$, 2.13 ± 0.11 $\mu\text{m}/\text{min}$ and 5.62 ± 0.35 $\mu\text{m}/\text{min}$ at a speed of 3000 $\mu\text{m}/\text{s}$, 1500 $\mu\text{m}/\text{s}$ and 1000 $\mu\text{m}/\text{s}$, respectively, and diminishes as the scanning speed continues to increase past these values. With a pulse energy of 150 nJ, a maximum etch rate of 7.00 ± 1.00 $\mu\text{m}/\text{min}$ is attained throughout a wide velocity range spanning from 750 $\mu\text{m}/\text{s}$ to 3000 $\mu\text{m}/\text{s}$, with the etch rate declining as the scanning speed decreases below 750 $\mu\text{m}/\text{s}$ or increases past 3000 $\mu\text{m}/\text{s}$. With the exception of the results obtained at 75-100 nJ and 3000 $\mu\text{m}/\text{s}$, the etch rate increases monotonically with the pulse energy and peaks at 150 nJ for both etchants, within the tested range and regardless of the translation velocity.

To understand this behaviour, the experimental results are compared to the observations made by Rajesh *et al* [118] who studied the influence of the net fluence on the etched length. This study was conducted while varying the ratio between the laser repetition rate and the translation velocity, which defines the number of incident pulses per unit area (the laser repetition rate was always kept below 1 MHz to prevent heat-accumulation effects). In particular, they observed that the etched length gradually increased with the deposited energy until reaching a maximum, above which, the etched length sharply decreased into a saturation value. These results were found to be independent of the laser repetition rate and suggest that the material response, in terms of structural modifications, gradually evolves with the deposited energy independently of the time interval between consecutive pulses. Accordingly, if the laser repetition rate and scanning speed are kept constant, then in a first regime it is expected that the etch rate increases with the pulse energy as was observed in figure 4.3. Further, Ross *et al* [122] also determined a steep rise in the etching selectivity for a pulse energy ranging between 120 nJ and 250 nJ, which was followed by a gradual decrease in the selectivity as the pulse energy grew beyond 300 nJ. Similarly, Hnatovsky *et al* [32, 33] also observed a

general increase of the longitudinal etch rate with pulse energy while writing with pulse durations spanning from 50 fs to 185 fs. Qi *et al* [124] added that the etch rate increased abruptly with the exposure energy density until reaching a maximum level that was kept for a wide interval, before decreasing for energy densities larger than 10-100 $\mu\text{J}/\text{m}^2$ depending on the translation velocity. All these results indicate that the generation of etching selectivity is mostly an energy accumulation effect, as has been proposed by the models presented by Hnatovsky *et al* [32] and by Bellouard *et al* [117]. In particular, these models predict that the nanogratings become more disordered and the nanoplanes start to interconnect with one another as the pulse energy grows thereby facilitating the diffusion of the etchant through the laser-irradiated volume, and that the increase in the deposited energy leads to a higher stress accumulated within the laser irradiated volume and to a higher densification which accelerate the etching reaction, respectively. Although a similar analysis regarding the evolution of the etch rate against the translation velocity could be made following the observations made in [118, 124], due to the narrow range of pulse energies and scanning speeds tested, no clear conclusions can be drawn. Lastly, writing at lower repetition rates (250 and 500 kHz) has been shown to enhance the etching selectivity, while weak etching was obtained when writing with repetition rates above 1 MHz probably due to thermal accumulation effects [122]. Further, Qi *et al* [124] also reported the formation of microbubbles and weak re-vetrification zones within the laser-irradiated volume at repetition rates higher than 1 MHz, which prevented selective etching. On the other hand, at low repetition rates (lower than 0.2 kHz) and translation velocities higher than 1 mm/s, the periodic nanostructures cease to be connected to one another which prevents selective etching. These observations highlight that the nanogratings form within a limited interval of laser repetition rates.

The results gathered in figure 4.3 also indicate that, regardless of the writing parameters, the etch rate is always higher when etching with HF acid instead of KOH, which point to a shorter etching reaction when using HF acid as chemical agent. However, this parameter is not the only one that needs to be accounted for. It is also important to consider the etch rate of the pristine medium in this analysis, as this will condition the aspect ratio (*i.e.* the ratio between the width and height) of the microfluidic channel. In figure 4.4, it is plotted the heat maps of the etching selectivity (S) for both etchants tested, which is defined as the ratio between the etch rate of the single-scan laser-exposure tracks (R_{wvg}) and the etch rate of pure fused silica (R_{silica}) according to equation 4.1.

$$S = \frac{R_{wvg}}{R_{silica}} \quad (4.1)$$

The trend displayed in both heat maps is similar for both etchants and summarizes the observations made earlier in figure 4.3. A higher selectivity is obtained when writing at larger pulse energies for a given translation velocity, and (in general) when scanning at higher speeds for a given pulse energy. It is also demonstrated that, in spite of the lower etch rate, a higher selectivity is obtained when etching with KOH instead of HF acid. For instance, a maximum selectivity of 4200 is obtained for a single-scan laser-exposure track written with a pulse energy of 150 nJ and scanning speed of 3000 $\mu\text{m}/\text{s}$ and etched with KOH, which is thirty times the maximum selectivity obtained when etching with HF

acid which equals 140 for a single-scan laser exposure track written with a pulse energy of 150 nJ and translation velocity of 4000 $\mu\text{m/s}$. The increase in etching selectivity with KOH over HF acid is not an unexpected result [38, 122]. Kiyama *et al* [38] have proposed that the formation of silica-rich structures and of oxygen-deficient centres within the porous nanolayers, which is attacked more easily by OH^- , is responsible for the enhanced selectivity with KOH. Meanwhile, Pépin *et al* [125] reported that this selectivity may be related to the formation of crystalline silicon within the modified silica, which etches up to three orders of magnitude faster than the pristine medium.

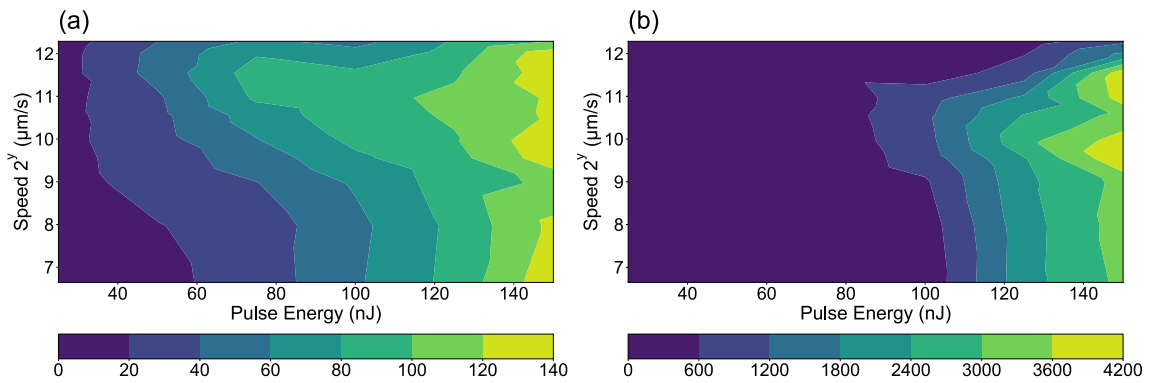


Figure 4.4: Etching selectivity map for single-scan laser-exposure tracks etched in (a) HF acid and (b) KOH.

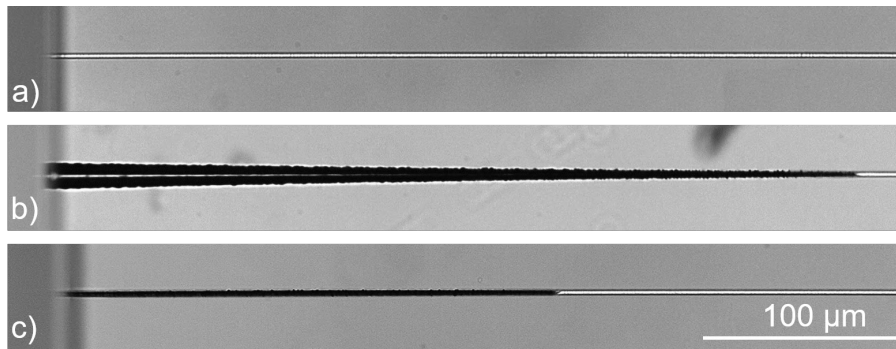


Figure 4.5: Top view images of single-scan laser exposure tracks written with a pulse energy of 125 nJ and translation velocity of 1000 $\mu\text{m/s}$ (a) after laser direct writing, and after chemical etching for 60 minutes in (b) HF acid and in (c) KOH. The channel is written from the left towards the right.

To comprehend how the different etching selectivities affect the profile of the microfluidic channel, figure 4.5 shows top view images of single-scan laser exposure tracks after laser direct writing (figure a) and after chemical etching for 60 minutes with HF acid (figure b) and with KOH (figure c). With HF acid as etchant, in spite of the longer etched length, the entrance of the microfluidic channel widens and it acquires a conical shape that translates into a non-uniform aspect ratio. The asymmetric growth is due to the entrance of the microfluidic channel being etched for a longer period of time than its end and due to the poor etching selectivity, similarly to what was described

in [126]. Meanwhile, a straight microfluidic channel with an almost constant aspect ratio and dimensions closer to the designed ones is obtained when etching with KOH, due to the higher etching selectivity. Still, it must be registered that tapering also occurs when etching with KOH; in particular, this effect could be easily seen if a centimetre-long microfluidic channel was fabricated due to the prolonged etching reaction. The results only show that this effect is less pronounced when etching with KOH rather than with HF acid. Additionally, other solutions can be implemented to compensate for the finite and/or lower etching selectivity. For instance, designing the microfluidic channel in a geometry that compensates for the limited selectivity can be used to overcome this issue [127]. In addition, He *et al* [126] were able to decrease the tapering angle by applying a post-etching glass drawing process, where the substrate was translated in relation to an oxyhydrogen flame which heated the sample to a temperature close to the melting point of fused silica; this approach has the added advantage of also decreasing the surface roughness of the microfluidic channel. In the case of microfluidic channels fabricated inside the fused silica substrate, several vertical outlets connecting the channel to the surface of the sample are generally written to surpass this issue [128].

To complement this analysis, it is also examined the distribution of nanogratings over the cross-section of the laser-modified volume and how it affects the etching reaction. Figure 4.6 shows the cross-section of single-scan laser-exposure tracks prior to etching for some of the tested writing conditions. An elliptically-shaped cross-section with major axis aligned with the direction of propagating of the fs-laser beam appears for all tested cases. As discussed in section 2.2.4, the width and height of the laser-induced modification can be estimated through the beam waist radius and Rayleigh length, respectively. In consequence, the 0.42NA focusing objective used in this work results in an asymmetrical modification elongated along the vertical direction, with the height being around 3.8 times the width. Further, the modification is also heterogeneous with two distinct regions being observed at the top and bottom of the cross-section. A darker region associated to a decrease in the refractive index and to the presence of nanogratings is noticed at the top of the modification, whereas a brighter region related to an isotropic increase of the refractive index is observed at the bottom of the cross-section. A similar profile has been reported elsewhere [109, 112]. Indeed, Hnatovsky *et al* [32] reported that the fraction of the laser-modified volume occupied by nanogratings is strongly affected by the relation between pulse energy and pulse duration. They observed that nanogratings cover the full extent of the smooth modification at pulse durations shorter than 130 fs and for pulse energies in-between 100 nJ and 1000 nJ, whereas by increasing the pulse duration to 185 fs the nanogratings became confined to the head of the cross-section while the tapered tip remained featureless.

In addition, figure 4.6 also reveals that the morphology of the laser-induced modification varies with the exposure parameters. The laser-induced modification is tenuous at 25 nJ, which in conjunction with the measurement of a weak etch rate at these pulse energies, indicates that the threshold for formation of nanogratings is around this value. With a pulse energy of 50 nJ and 75 nJ, the laser-induced modification starts to

fade as the translation velocity increases. In fact, when increasing the scanning speed while keeping the pulse energy constant, the cross-section gets narrower and the size of the damage track's head decreases, probably due to the lower net fluence and reduced number of incident pulses. Meanwhile, increasing the pulse energy, while maintaining the translation velocity fixed, seems to increase the height of the laser-induced modification, akin to what had been reported in [32, 33, 124].

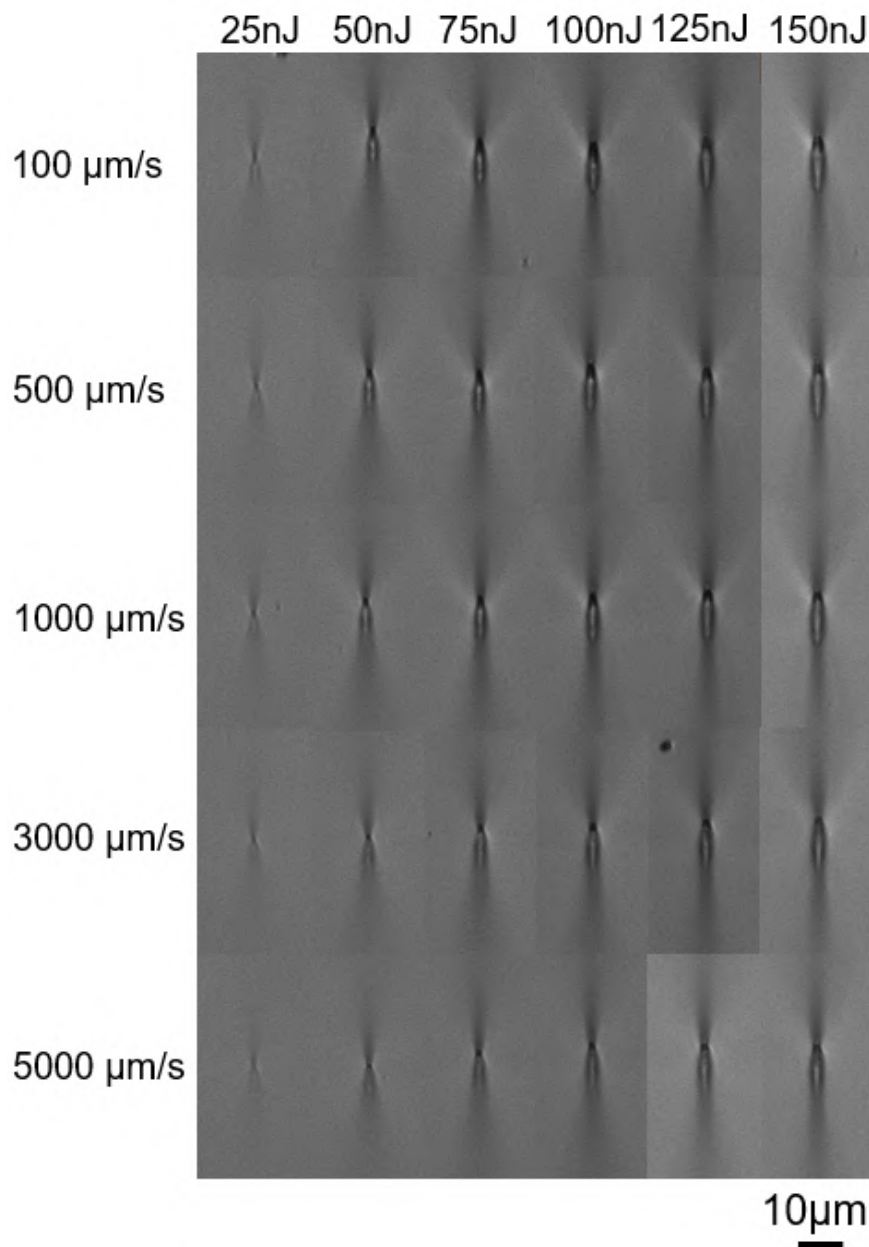


Figure 4.6: Cross-section of single-scan laser exposure tracks after laser direct writing against pulse energy and scanning speed. The fs-laser beam is incident from the top.

The cross-section profile of the laser-induced modification during the chemical etching reaction in HF acid is depicted in figure 4.7. It is observed that the entire cross-section has been etched after 10 minutes, regardless of the pulse energy and translation velocity used to write the laser-exposure tracks. Still, the irradiation conditions lead to some differences

regarding the morphology of the etched area.

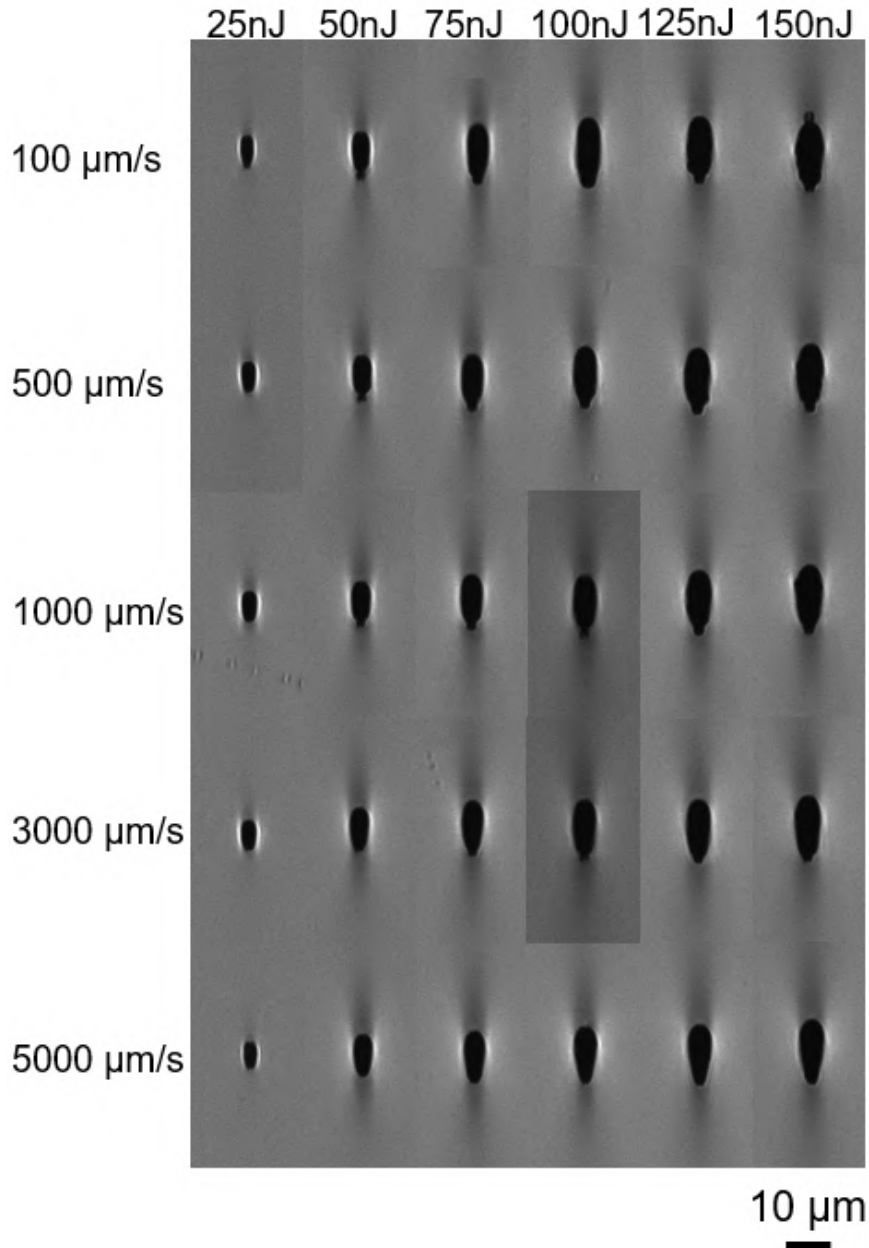


Figure 4.7: Cross-section of single-scan laser exposure tracks after chemical etching in HF acid for 10 minutes against pulse energy and scanning speed. The fs-laser beam is incident from the top.

The cross-section seems to be symmetric when writing with a pulse energy of either 25 nJ and independent of the translation velocity, whereas it becomes asymmetric as the pulse energy increases from 50 nJ upwards. In particular, for pulse energies equal to or higher than 50 nJ, the head of the irradiated region is round-shaped whereas its tail shows a velocity-dependent profile. For example, with a pulse energy of 50 nJ, the bottom part of the etched cross-section seems to be deformed for translation velocities lower than 1000 $\mu\text{m/s}$ while it becomes arrow-shaped as the scanning speed increases from 2000 $\mu\text{m/s}$ upwards. It is also observed that the etched profile becomes more symmetric,

evolving into a round-shaped one as the translation velocity keeps growing. Although this trend is observed when writing at pulse energies of 50 nJ or higher, the scanning speed at which the transition from a deformed into an arrow-shaped profile occurs also increases with the pulse energy. Moreover, the HF acid circulating inside the microfluidic channel also starts to etch isotropically the pristine layers surrounding the etched volume, which causes the cross-sectional area to expand radially and to become more symmetric and rounder as the etching reaction is prolonged, as shown in figure 4.8(a).

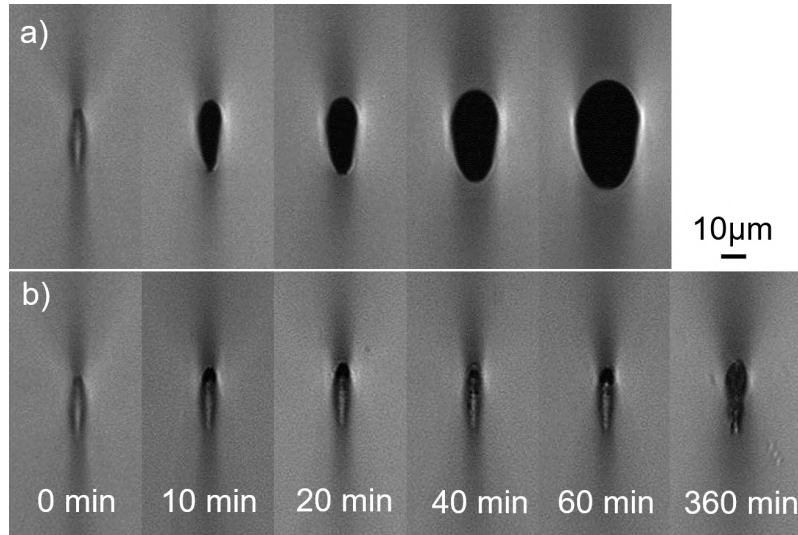


Figure 4.8: Evolution of the cross-section profile of single-scan laser-exposure tracks written with a pulse energy of 150 nJ and translation velocity of 3000 $\mu\text{m/s}$ when etched in (a) HF acid and (b) KOH.

On the other hand, a dissimilar effect is observed when etching with KOH. After 10 minutes of etching, only the regions associated to the presence of nanogratings, *i.e.* the head of the laser-exposure track or, in rare cases, the defects present at the tail end of the cross-section, have been etched while the regions related to an isotropic increase of the refractive index seem to be intact. In fact, even after 360 minutes of etching, the cross-section of some laser-exposure tracks had yet to be entirely etched, as illustrated in figure 4.8(b). Although this seems to be a disparate behaviour than what was observed for the laser-exposure tracks etched with HF acid, it should be noted that the clearer regions (in the cross-section images taken after laser direct writing) are associated to an isotropic increase of the refractive index which contain a high number of three-membered Si–O–Si ring structures that is known to be etched at a faster rate than the six-membered rings defining the pristine medium. However, while these regions are etched faster with HF acid, due to the occurrence of nucleophilic attack by F^- on the silicon atom simultaneously with the electrophilic attack by proton on oxygen atom [38], the reactivity of KOH species is much lower which results in a slower etching. At the same time, based on these observations, it must be highlighted that the results shown in figures 4.3 and 4.4 concerning the longitudinal etch rate of single-scan laser-exposure tracks may correspond to the etch rate of the top regions (containing nanogratings) of the modified volume.

In all, for a repetition rate of 500 kHz, the cross-section of the laser-irradiated region consists of two distinct modifications, one located at the top related to the presence of nanogratings and another at the bottom associated to the isotropic increase of the refractive index, which are etched at different rates. Consequently, in spite of the higher selectivity, only the head of the cross-section is removed at a high enough rate when performing the etching reaction with KOH, while the tail is etched at a pace similar to the pristine etch rate. In turn, the chemical etching reaction has to be prolonged to a matter of hours in order to etch the entire laser-modified volume, which increases the fabrication time. Meanwhile, when etching with HF acid, the entire modified volume is quickly removed which translates into a more uniformly etched cross-section. Still, although a maximum etch rate is obtained at higher pulse energies, this also results in a damaged and asymmetric cross-section profile. A more symmetrical and rounder cross-section is obtained when writing at lower pulse energies and higher translation velocities. Further, the laser-exposure tracks can be written at high scanning speeds without compromising the longitudinal etch rate, which also aids in minimizing the duration of the laser direct writing process. Lastly, it has been suggested that a higher etch rate and a more uniformly etched volume can be obtained if the entire cross-section of the laser-irradiated volume is filled with nanogratings, which can be achieved either by lowering the laser repetition rate to 200-300 kHz [124] or by shortening the duration of the laser pulses to below 130 fs [32]. At the same time, in order to increase the fabrication throughput and in the context of mass-production, irradiation with high repetition rate laser sources is more appealing.

4.3 Etching of Multiple-Scan Laser-Exposure Tracks

The design of the device is changed in order to fabricate wider microfluidic channels, being adopted the writing scheme shown in figure 4.2 which enables the formation of straight rectangular-shaped and three-dimensional channels at the surface or embedded in the substrate. In this approach, the layout of the microfluidic channel is formed by multiple laser-exposure tracks periodically arranged along the horizontal and/or vertical directions. The centre of the laser-exposure tracks composing each horizontal plane are separated by a constant gap dy , where the centre-to-centre distance between two consecutive layers is defined by dz . All laser-exposure tracks are written by scanning the sample along the +X direction relative to the focus of the fs-laser beam, in order to prevent inhomogeneities related to the “Quill” effect, and the horizontal planes are scanned from the bottom towards the surface of the substrate to avoid writing over previously exposed tracks. In addition, the polarization of the fs-laser beam is always orthogonal to the scanning direction to have the nanogratings aligned with the axis of the device. The length of the microfluidic channel matches the length of the individual laser-exposure tracks, and the channel possesses a rectangular-shaped cross-section. Its width equals the number of laser-exposure tracks in each plane times the gap dy plus the width of an individual laser-exposure track, whereas its height is given by the number of horizontal planes times the gap dz plus the height of an individual laser-exposure track.

As studied by Bellouard *et al* [129], the density of laser-exposure tracks, as well as the writing sequence, affects the etching dynamics. Therefore, to understand the influence of the gaps dy and dz , and to calibrate the writing and etching procedures, two sets of microfluidic channels are fabricated. According to figure 4.2, in one set several microfluidic channels are fabricated each consisting of four single-scan laser exposure tracks written at a depth of 100 μm and with a specific separation dy ranging from 1 to 8 μm , whereas in the other set multiple microfluidic channels composed by four single-scanned laser-exposure tracks were written at a centre depth of 100 μm and with a given gap dz that spanned from 1 to 15 μm . The influence of the pulse energy and of the translation velocity was again studied by writing various microfluidic channels within each set, each with a unique pulse energy and scanning speed that ranged from 60 nJ to 120 nJ and from 250 $\mu\text{m/s}$ to 4000 $\mu\text{m/s}$, respectively. Two replicas of each set were also fabricated, one to be etched in HF acid and the other to be etched in KOH, in order to assess the effect of the etchant as well. After laser direct writing and mechanical polishing, each set was etched in its respective solution. The etching reaction was stopped at times to evaluate the morphology of the microfluidic channel under an optical microscope. The cumulative etching time was 60 minutes when etching with HF acid and 360 minutes when etching with KOH.

Figures 4.9 and 4.10 show the cross-section of the laser-modified region after laser direct writing for different pulse energies, translation velocities and separations along the horizontal plane dy . It is observed that all laser-exposure tracks merge with a gap of 1 μm regardless of the pulse energy and translation velocity, whereas for the other values of dy tested the individual laser-exposure tracks can be easily distinguished from one another. Starting at a gap of 3 μm for pulse energies between 60 nJ and 100 nJ and at a gap equal to 4 μm for a pulse energy of 120 nJ, it is also visible that there is a pristine layer in between the individual laser-exposure tracks. At specific irradiation dose levels and at certain gaps dy , the tail of the cross-section of the laser-modified volume is damaged and exhibits what appear to be cracks. For a gap of 1 μm or 2 μm , these fractures appear at all pulse energies tested and for a translation velocity in-between 250 $\mu\text{m/s}$ and 1000 $\mu\text{m/s}$. Meanwhile, for a gap equal to 3 μm , cracks only appear until scanning speeds of 500 $\mu\text{m/s}$ and 1000 $\mu\text{m/s}$ for pulse energies of 60 nJ or in-between 80 and 120 nJ, respectively. As the gap dy increases, the processing window in which cracks are not visible seems to extend. For a gap dy equal to 4 μm or 5 μm , the fractures are only observed for a pulse energy of 80 nJ or higher and for translation velocities lower than or equal to 500 $\mu\text{m/s}$. No cracks are visible for the microfluidic channels formed with an horizontal spacing dy between 6 μm and 8 μm . These results show that the appearance of cracks is more likely: (i) at high pulse energies, (ii) at low scanning speeds which leads to an increase in the deposited energy due to the higher number of incident pulses, and (iii) at low separations between laser-exposure tracks due to an over-writing effect. Hnatovsky *et al* [32] also reported that irregular cracks appeared around the tip portions of the modification when increasing either the pulse energy and/or the pulse duration as a result of the accumulated stress within the laser-modified volume. Rajesh *et al* [118] also

observed that stress would build up at the tip of the elliptical cross-section by continuously increasing the deposited energy on the irradiated volume. When the local stress becomes too high, the stored elastic energy and accumulated stress would relax under the form of a crack that propagates through the high-stress zone.

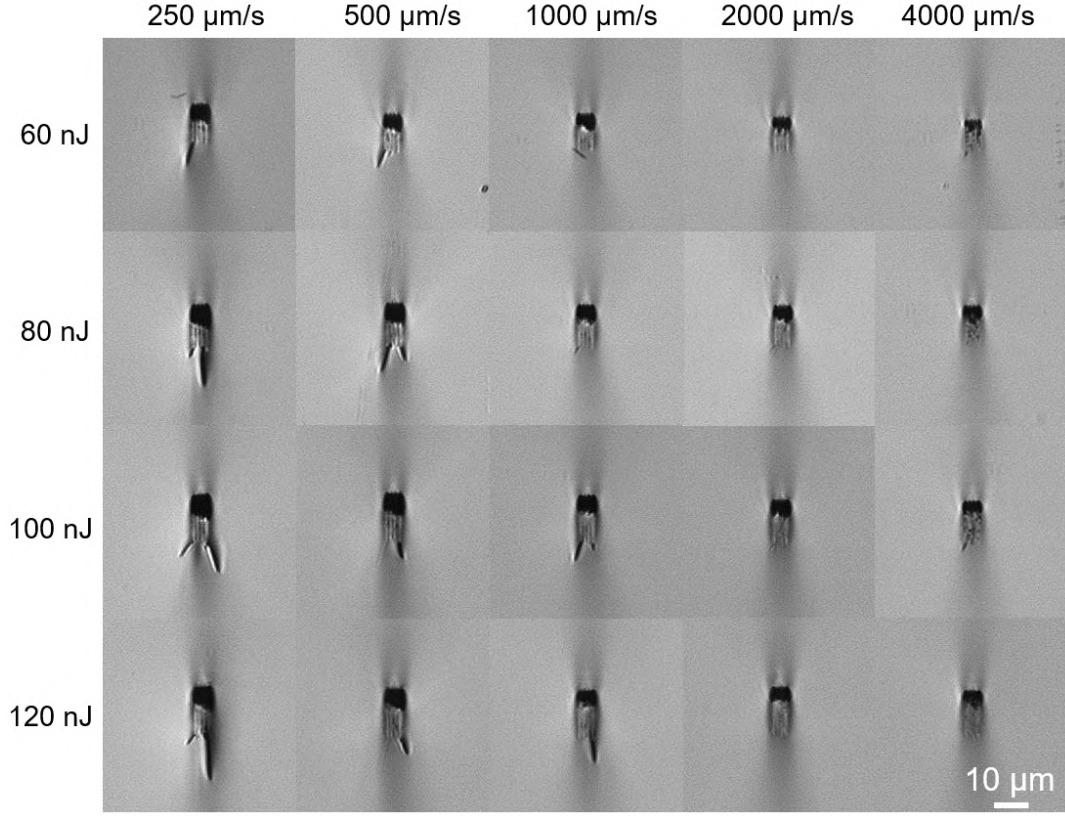


Figure 4.9: Cross-section of multiple-scan laser exposure tracks, horizontally spaced by 1 μm , after laser direct writing against pulse energy and scanning speed. The fs-laser beam is incident from the top, and the scans are written from right to left.

Consequently, the appearance of cracks already narrows down the processing window for obtaining uniformly etched and crack-free microfluidic channels. Figures 4.10 and 4.11 depicts the cross-sectional profile of the microfluidic channels during the etching reaction with HF acid and with KOH, respectively. Considering the etching reaction with HF acid, it is observed that the longitudinal etch rate slightly increases for the microfluidic channels written with a gap dy of 1 μm and 2 μm , whereas it remains equal to the etch rate of the single-scan laser exposure tracks for the larger separations. This suggests that, for gaps of 2 μm or lower, the fs-laser beam writes over pre-existent laser-exposure tracks which further changes the composition of the laser-modified volume, alike to what has been observed in [129] where it is proposed that build-up of stress around the laser-affected zones alters the etch rate. In addition, the entire cross-section of the microfluidic channels written with a gap dy of 1 μm or 2 μm is etched after only ten minutes of etching. For the larger gaps dy , the reaction needs to be extended in order for the individual laser-exposure tracks to merge and to obtain a uniformly etched microfluidic channel. To reach this situation for a gap of 3 μm , 4 μm , 5 μm and 6 μm the etching reaction needs to last 20, 30,

40 and 50 minutes, respectively. Further, it is also observed that merging occurs faster when writing at higher pulse energies due to the cross-section being slightly larger, with no significant variations being visible when changing the translation velocity. However, in spite of eventually merging, the surface roughness of the top and bottom walls of the microfluidic channel significantly depends on the gap dy . As evidenced in figure 4.10, the walls become more rugged when increasing the separation between laser-exposure tracks, and tend to smooth as the etching reaction is prolonged due to the HF acid etching the pristine medium in between the individual laser-exposure tracks. The top view images also reveal that the microfluidic channel evolves from a darker to a clearer colouration as the surface roughness decreases.

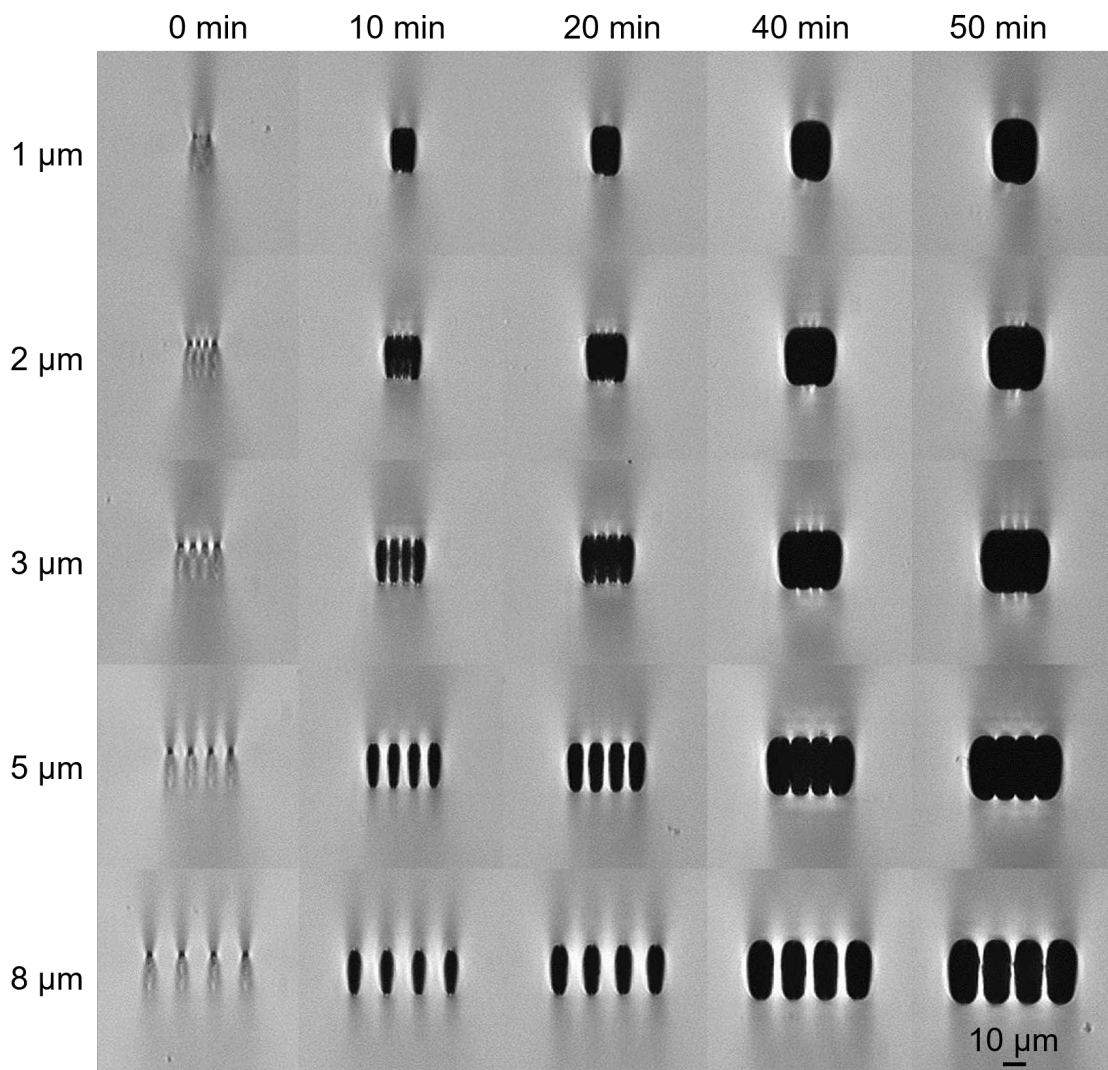


Figure 4.10: Evolution of the cross-section of multiple-scan laser exposure tracks, written with a pulse energy of 80 nJ and translation velocity of 4000 $\mu\text{m/s}$ and etched in HF acid, against the horizontal gap dy . The fs-laser beam is incident from the top, and the scans are written from right to left.

Meanwhile, when employing KOH as etchant, only the top section of the microfluidic channel (which contains nanogratings) is etched after a period of 60 minutes, regardless

of the pulse energy, translation velocity or separation between laser-exposure tracks used. Moreover, due to the etch rate of the pristine medium being much lower than when using HF acid as etchant, merging between laser exposure tracks requires a longer reaction. In fact, even after an etching period of 360 minutes the individual laser-exposure tracks had yet to merge for a respective separation of 3 μm or higher.

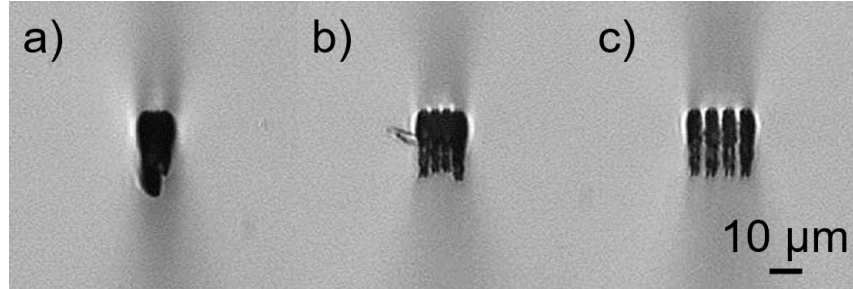


Figure 4.11: Cross-section of multiple-scan laser exposure tracks, written with a pulse energy of 80 nJ and translation velocity of 4000 $\mu\text{m/s}$ and etched in KOH for 360 minutes, for an horizontal gap dy of (a) 1 μm , (b) 2 μm and (c) 3 μm . The fs-laser beam is incident from the top, and the scans are written from right to left.

Focusing now on the microfluidic channels written while spacing the laser-exposure tracks along the Z direction, in figure 4.12 it is observed that the individual tracks overlap one another for gaps dz equal to or lower than 8 μm while a pristine layer is visible in between tracks for gaps of 10 μm or higher. This result is expected given the elongated profile of a single laser-exposure track which translates into a higher spatial resolution along this direction. Regardless of the gap dz , cracks are visible at the bottom of the cross-sectional images for the microfluidic channels written with a pulse energy between 80 nJ and 120 nJ and with a translation velocity ranging from 250 $\mu\text{m/s}$ to 500 $\mu\text{m/s}$. Again, these observations narrow the processing window and imply that lower pulse energies and/or higher translation velocities must be used to obtain defect-free microfluidic channels, similarly to what was discussed in the previous paragraphs. When using HF acid as etchant, it is observed that the entire cross-section of microfluidic channels with a gap dz up to 10 μm is etched within the first 10 minutes of the etching reaction. Meanwhile, for a gap dz equal to 15 μm , the laser-exposure tracks written with a pulse energy of 100 nJ or 120 nJ only merge after 20 minutes, while those written with a pulse energy of 80 nJ and 60 nJ only merge after 40 and 50 minutes of etching, respectively. This result is expected because, for this separation dz , the individual tracks do not overlap one another. Again, merging between laser-exposure tracks is quicker when the microfluidic channel is written with a higher pulse energy, whereas it seems independent from the scanning speed. Further, the sidewalls of the microfluidic channels written with a gap dz lower than or equal to 6 μm are straight during the entire etching reaction. On the other hand, with a vertical separation dz of 8 μm or 10 μm , the sidewalls are corrugated during the first twenty minutes of etching, and grow into a straight and smooth profile as the etching reaction is extended. Regardless of the pulse energy, translation velocity or gap dz used, it is also observed that the

microfluidic channel is rounder on top, whereas it possesses a dose-dependent profile on its bottom. Indeed, the bottom surface of the microfluidic channel grows from an arrow to a rounder shape as the scanning speed increases or by extending the etching reaction, similarly to what was concluded for the individual laser-exposure tracks. When etching with KOH, a different cross-section profile is obtained, analogous to what was discussed for microfluidic channels formed by spacing the laser-exposure tracks along the horizontal plane. For a gap dz lower than or equal to $6\text{ }\mu\text{m}$, where the laser-exposure tracks overlap one another, the reaction is still incomplete even after 360 minutes as the cross-section images reveal that some regions are still to be etched, which arises from the nanogratings not filling the entire laser-modified volume. Similarly, given that the etch rate of the pristine medium is much lower when etching with KOH than with HF acid, merging between laser-exposure tracks vertically spaced by $8\text{ }\mu\text{m}$ or $10\text{ }\mu\text{m}$ only occurs after 240 minutes of etching, as opposed to the 10 minutes required when etching with HF acid.

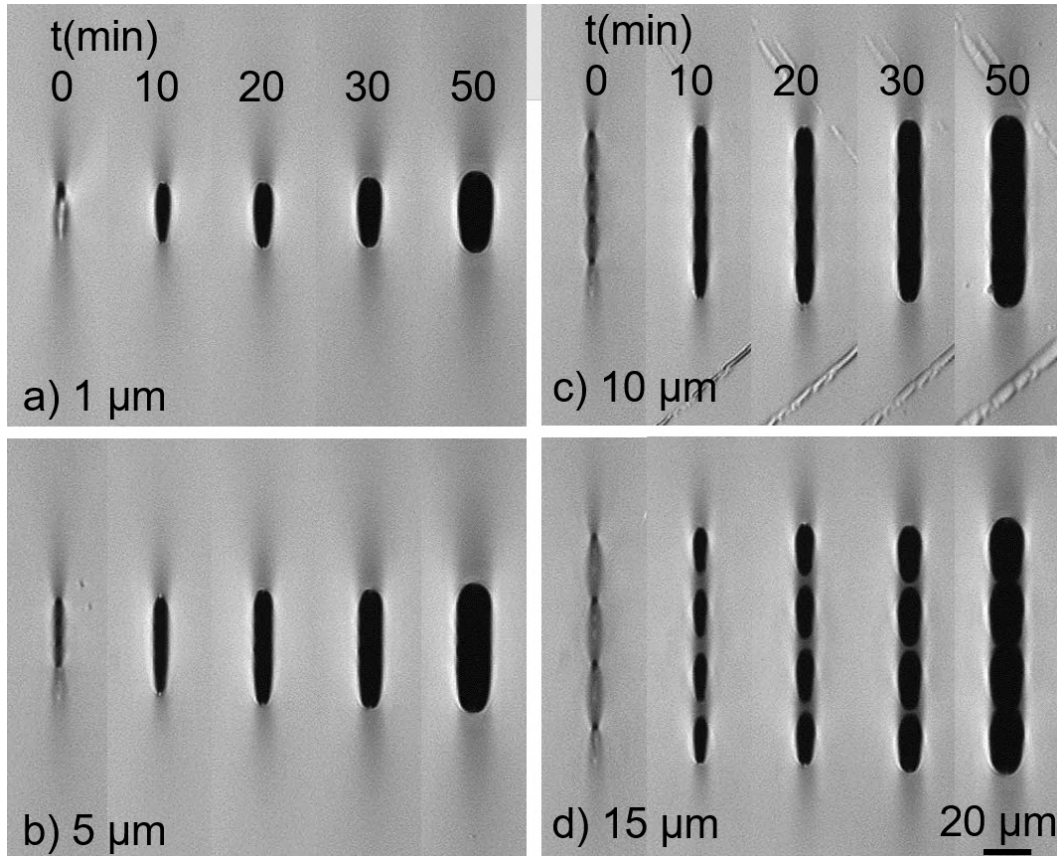


Figure 4.12: Evolution of the cross-section of multiple-scan laser exposure tracks, written with a pulse energy of 80 nJ and translation velocity of $4000\text{ }\mu\text{m/s}$ and etched in HF acid, for a vertical gap dz of (a) $1\text{ }\mu\text{m}$, (b) $5\text{ }\mu\text{m}$, (c) $10\text{ }\mu\text{m}$ and (d) $15\text{ }\mu\text{m}$. The fs-laser beam is incident from the top, and the scans are written from bottom to top.

In all, etching with HF acid instead of KOH provides a more uniformly etched cross-section, while also enabling writing with larger separations dy and dz without compromising merging between the individual laser-exposure tracks. Further the vertical spacing dz can be larger than the horizontal spacing dy , owing to the elongated profile

of the laser-exposure tracks along the vertical direction which provides a higher spatial resolution. Still, to prevent the appearance of cracks, the laser-exposure tracks cannot be written at high pulse energies and/or at low translation velocities or with a short gap in between them. On the other hand, the separation between laser exposure tracks cannot be much higher than the width or height of an individual single-scan track, as this would translate into a microfluidic channel with rugged walls.

Still, these results were obtained while performing the etching reaction from the side facet of the substrate. In most cases, the microfluidic channel is made at the surface of the substrate with the etching reaction proceeding in a different way. Instead of the etchant diffusing simultaneously through all the laser-exposure tracks terminating at the facet of the substrate, the horizontal layers are now removed sequentially as the etchant etches through the surface of the substrate towards the bottom of the microfluidic channel. To assess the differences in the etching dynamics drawn by the change in the writing scheme, two similar sets of devices are fabricated with one to be etched in HF acid and the other in KOH. In each set, several microfluidic channels are fabricated by stacking multiple laser-exposure tracks, each written with pulse energy of 60 nJ, a translation velocity of 3000 $\mu\text{m/s}$ and with the polarization of the fs-laser beam orthogonal to the scanning direction; these conditions ensure that no fractures are formed. All laser-exposure tracks are written by scanning the substrate along the +X direction relative to the laser focus to prevent the “Quill” effect. The horizontal gap dy between laser-exposure tracks is 3 μm , whereas the vertical spacing dz varies between microfluidic channels and ranges from 1 μm to 15 μm . In the end, several 500 μm long microfluidic channels with rectangular cross-section with 40 $\mu\text{m} \times 120 \mu\text{m}$ (width by height) are designed. The microfluidic channels were also written 40 μm from a pre-polished border of the substrate, to enable monitoring of the cross-section profile during the etching reaction while avoiding energy depletion effects related to focusing mismatch at the edge of the sample. Similarly to what was previously described, the etching reaction is stopped at times to inspect the profile of the microfluidic channel. After laser direct writing, the surface of the laser-modified area is ablated as expected given that the energy threshold for ablation is lower at the surface of the substrate than at its bulk.

The cross-section profile images collected during chemical etching for the devices etched in HF acid are shown in figure 4.13. Regardless of the gap dz tested, it is concluded that as the etchant diffuses through the vertically aligned laser-exposure tracks, it also starts to etch the pristine layers horizontally separating these tracks which leads to them merging later on. Still, despite this general trend, the used separation dz causes some slight differences in the etching dynamics. The etchant reaches the bottom of the microfluidic channel after 30 minutes for a gap dz equal to 1 μm , whereas it requires 45 minutes for separations between 2 μm and 8 μm and 75 minutes for a gap of 10 μm ; with a gap of 15 μm the etching still remained incomplete after 180 minutes. Consequently, a vertical etch rate of around 4 $\mu\text{m/min}$ is obtained for a gap dz equal to 1 μm , which decreases to 2.7 $\mu\text{m/min}$ for a separation between 2 μm and 8 μm and to 1.6 $\mu\text{m/min}$ with dz equal to 10 μm . A higher vertical etch rate and selectivity are then obtained when

closely stacking the laser-exposure tracks along Z, probably due to a higher accumulation of stress within the laser-modified volume when using smaller gaps dz . For comparison, Ross *et al* [122] observed that the etch rate of microfluidic channels, designed following the same writing scheme, remained constant for scan separations up to 7 μm and 10 μm when etching with KOH and HF acid, respectively. Moreover, they also concluded that the vertical etch rate is higher when writing with the polarization of the fs-laser beam orthogonal to the writing direction.

Nonetheless, the etching reaction does not end when the HF acid reaches the bottom of the microfluidic channel, needing to be extended in order for the intermediate pristine layers to be etched and to decrease the surface roughness of the inner walls. As demonstrated in figure 4.13, as the horizontally separated laser-exposure tracks merge with one another, the surface of the microfluidic channel evolves from rugged to flat with its roughness decreasing as the etching time is prolonged, as it had also been reported in [32, 130]. For a separation dz equal to 1 μm the bottom surface is flat after 90 minutes, whereas for gaps between 2 μm and 8 μm it is only even and uniform after 120 minutes of etching. Additionally, regardless of the vertical separation between laser-exposure tracks used, the edges at the bottom of the microfluidic channel remain round. As it will be explained in more detail in chapter 6, the RMS roughness of the bottom surface of the microfluidic channel decreases with the gap dy , equalling 86.7 nm, 149.2 nm and 229.9 nm for track separations of 3 μm , 4 μm and 5 μm , respectively. Although the surface roughness should further decrease if the separation between laser-exposure tracks is reduced, this would lead to the formation of cracks at the bottom of the microfluidic channel.

Regarding the sidewalls of the microfluidic channel, these are straight and smooth for a gap dz between 1 μm and 6 μm , whereas they are corrugated for a separation of either 8 μm or 10 μm due to a smaller overlap between laser-exposure tracks obtained under these conditions. Sikorski *et al* [130] studied with more detail the surface quality of the sidewall of microfluidic channels fabricated following a similar procedure, and concluded that the sidewall surface shows “fish-scale”-like features that can be correlated to the laser-exposure tracks. They also added that a minimum RMS roughness of 20 nm to 30 nm is obtained if the vertical gap dz is between 0.5 μm and 4 μm . Additionally, a higher roughness is obtained if the scanning direction is perpendicular to the surface or if the fs-laser beam is polarized parallel to the scanning direction due to the alignment of the nanogratings. It is also observed that the roughness of the sidewalls is lower than that of the surface of the microfluidic channel, which is attributed to the larger spatial resolution following from the elongated profile of the laser-exposure track. Still, the surface roughness can be decreased to a nanometric scale either by performing thermal annealing [128] or by glass drawing with an oxyhydrogen flame [126] after chemical etching; in particular, thermal annealing will be discussed in more detail in chapter 6.

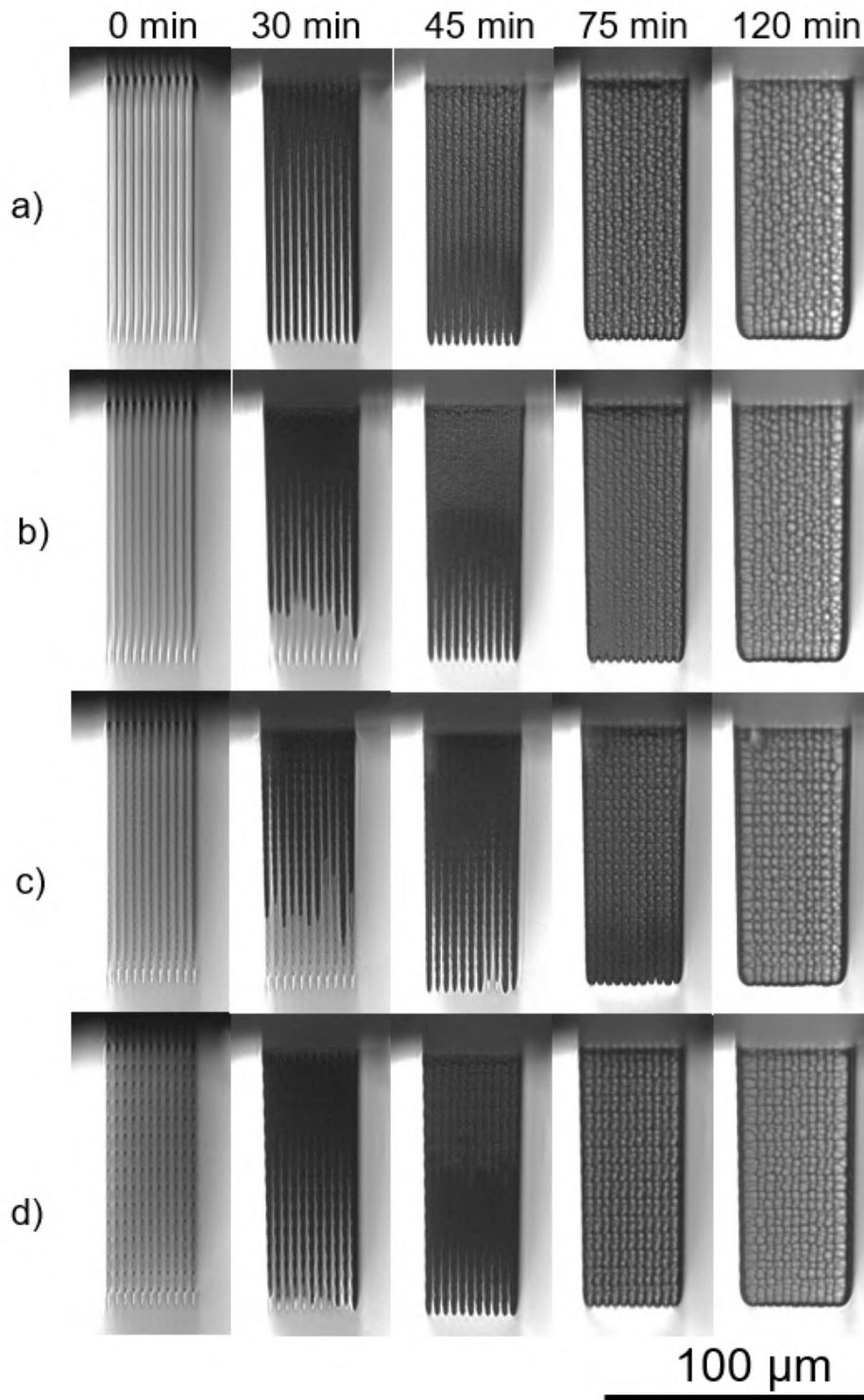


Figure 4.13: Evolution of the cross-section of microfluidic channels when etched in HF acid. The channels are written with a pulse energy of 80 nJ, translation velocity of 4000 $\mu\text{m/s}$ and horizontal gap dy of 3 μm , while the vertical spacing dz is (a) 1 μm , (b) 3 μm , (c) 5 μm and (d) 8 μm . The fs-laser beam is incident from the top, while the modified planes are written from bottom to top and the laser-exposure tracks within each plane are written from right to left.

During chemical etching, it is also observed that the width of the microfluidic channel increases at a pace equal to the etch rate of fused silica, and that the channel is slightly

tapered due to the limited etching selectivity. In particular, the microfluidic channels formed with a vertical gap dz between 1 μm and 6 μm exhibit an angular deviation from the Z direction of 1.4° , which translates into a 6 μm width variation between the top and bottom of the channel.

Although the duration of the etching reaction can be shortened by a few minutes and the surface roughness of the microfluidic channel can be lowered by decreasing the gaps dy and dz , this is done at the expense of a higher number of laser-exposure tracks which extends the duration of the laser direct writing process by a few hours. At the same time, the risk of fractures at the bottom of the microfluidic channel increases by tightly packing the laser-exposure tracks. Therefore, to minimize the fabrication time while still obtaining a microfluidic channel with straight sidewalls and a smooth surface, the horizontal and vertical gaps dy and dz should be around 2 μm and 3 μm and 5 μm and 6 μm , respectively, when etching with HF acid. The duration of the laser direct writing process can also be reduced by increasing both the translation velocity and the laser repetition rate evenly in order to maintain a constant net fluence [32, 105]. Still, by increasing the repetition rate, the formation of nanogratings covering the entire cross-section of the irradiated volume may be compromised due to thermal accumulation effects. Figure 4.14 shows top and cross-section images of a microfluidic channel fabricated at optimal conditions, where the inner walls are smooth and straight (tapering angle lower than 1°) while no cracks are observed.

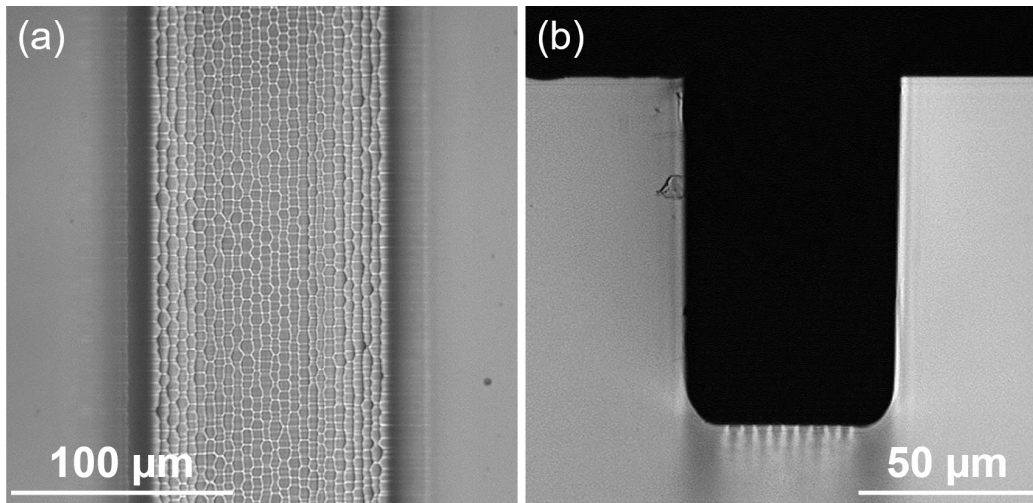


Figure 4.14: (a) Top view and (b) cross-section image of a microfluidic channel after etching in HF acid for 60 minutes. The channel was written with a pulse energy of 60 nJ, translation velocity of 3000 $\mu\text{m/s}$, and horizontal and vertical gaps dy and dz of 3 μm and 5 μm , respectively. The cross-sectional image was obtained after polishing the facet of the substrate until exposing the entrance of the microfluidic channel.

Regarding the sample etched in KOH, it is observed that the etching reaction is still incomplete even after ten hours regardless of the chosen gap dz . This is again related to the fact that the cross-section of the laser-irradiated volume is not solely composed by nanogratings, but it also contains regions associated to an isotropic increase of the refractive index that etch slowly at a rate similar to the etch rate of the pristine medium. The

long etching time nulls the selectivity advantage presented by KOH, which, in conjunction with the results displayed throughout this chapter, means that the etching reaction should be done with HF acid.

4.4 Conclusion

The goal of this chapter was to understand the influence of the irradiations parameters and of the etchant on the fabrication of microfluidic channels in fused silica. Based on these results, the correct fabrication parameters, essential for the design of the optofluidic devices presented throughout this dissertation, were determined. Here, it was considered the fabrication of rectangular-shaped microfluidic channels designed by stacking laser-exposure tracks along the horizontal and vertical directions with a constant spacing in-between tracks.

With a laser repetition rate of 500 kHz, the cross-section of the laser-irradiated volume consists of two distinct regions regardless of the pulse energy or translation velocity used. The head of the modification contains nanogratings which are etched at a higher rate due to their composition, whereas at its tail the laser-induced modification is associated to an isotropic increase of the refractive index which is etched at a pace slightly higher than the pristine medium due to the denser network of modified fused silica. In spite of the distinct etch rates associated to both laser-induced modifications, the entire cross-sectional area is etched when performing this reaction with HF acid. With KOH as etchant, only the head of the laser-irradiated volume is etched in suitable time which results in a highly asymmetric and irregular microfluidic channel. For these reasons, it was concluded that the etching should be performed with HF acid instead of KOH.

Overall, the key factor in achieving a higher etch rate of laser-modified silica is the formation of nanogratings aligned along the scanning direction. Still, the design parameters and the writing conditions are also known to condition the formation of microfluidic channels. Several trade-offs need to be made in order to minimize the duration of the laser direct writing procedure while preserving a high etch rate and selectivity and enabling the formation of smooth and crack-free microfluidic channels. In short, a higher longitudinal etch rate is obtained by writing with more energetic beams or by decreasing the gap between laser-exposure tracks. However, these conditions can also lead to fractures formed at the bottom of the microfluidic channel due to the release of accumulated stress. This type of damage can also occur if a lower translation velocity is used, having also observed that the etched profile evolves from an arrow to a round-shape as the scanning speed increases. Further, by decreasing either the horizontal or vertical separation between laser-exposure tracks, the duration of the etching reaction can be shortened and smoother inner walls can be realized, at the expense of a much longer writing process and with the added risk of fractures. Taking all of these factors into account, it is concluded that, for writing at 500 kHz, the inscription conditions should be: pulse energy of 60 nJ, translation velocity of 3000 $\mu\text{m/s}$, fs-laser beam linearly polarized with polarization set orthogonal to the scanning direction, and horizontal and

vertical gaps between adjacent tracks of 3 μm and 5 μm , respectively. These conditions minimize the writing time, provide a high enough etch rate (longitudinal and vertical etch rates of 12 $\mu\text{m}/\text{min}$ and 2.7 $\mu\text{m}/\text{min}$, respectively) and ensure that the inner walls are smooth with no cracks being observed at the surface of the microfluidic channel. In particular, the surface roughness is smaller along the sidewalls as a result of the elongated laser-exposure track, and can be improved by prolonging the etching reaction. With these parameters, tapering of the microfluidic channels, which is inherent to this fabrication method due to the limited etching selectivity, is also minimized with the sidewalls being straight and revealing a maximum deviation of 1° from the normal.

Despite determining the fabrication process for the production of straight rectangular-shaped microfluidic channels (which compose the optofluidic devices presented in the following chapters), some improvements can still be made. For instance, a higher etch rate and selectivity can be obtained if the cross-section of the laser-modified volume is entirely composed by nanogratings, which can be realized by decreasing either the pulse duration or the laser repetition rate. In addition, although the proposed writing scheme enables the formation of other geometries, the design of curved paths may be hindered when writing with static polarization due to the nanogratings ceasing to be aligned with the axis of the microfluidic channel which leads to a decrease in the etch rate. This issue can be solved by dynamically rotating the laser polarization during the inscription process to guarantee that the nanograting planes are always periodic to the surface normal [122], or by writing with a circularly polarized beam due to the random alignment of the nanogratings which renders a spatially-uniform etch rate [32]. Lastly, the microfluidic channels reported in this chapter and throughout the dissertation are formed at the surface of the substrate, which demands an additional sealing step to close the channel either by fs-laser welding of a glass cover to the substrate containing the channel or by irreversibly bonding a PDMS layer to the fused silica substrate. Other approach is to also form the microfluidic channels embedded in the fused silica substrate, with two (or more) access holes linking the channel to the surface of the substrate and enabling the etchant to diffuse through the modified volume.

Chapter 5

Fabry-Pérot Interferometers and Magnetic Field Sensing

This chapter discusses the fabrication of a Fabry-Pérot interferometer in a planar fused silica substrate and its potential as an optical sensor for measurement of magnetic field. The device is composed by a microfluidic channel, which operates as the etalon and which is filled with the analyte of interest, while being probed by a fs-laser written optical waveguide formed orthogonal to the cavity. The influence of the design parameters on the spectral properties of the measured signal are evaluated. In particular, it is studied how the loss mechanisms of fs-laser written waveguides affect the measured signal-to-noise ratio and the finesse of the device, and it is considered how the correct choice of the exposure parameters of the microfluidic channel can minimize mirror imperfections (namely, surface roughness and tilted interfaces). Besides being used as a refractometer, the interferometer is also tested as a magnetic field sensor based on the field-dependent refractive index property of magnetic fluids that are injected within the microfluidic channel. Operation as an optical sensor relies on tracking the position of the resonant wavelength, which shifts whenever the refractive index of the liquid within the cavity changes. Strategies for sealing the microfluidic channel are also considered.

5.1 Introduction

In its most basic form, a Fabry-Pérot interferometer corresponds to a standing-wave resonator consisting of an optical cavity, formed by a solid or fluidic medium, made in-between two parallel partially reflecting mirrors separated by a certain distance. Light launched into the resonator travels multiple times within the cavity while being partially transmitted when reaching each of the interfaces. The superposition of the waves transmitted across either interface leads to a modulated output signal, whose properties depend on the width and refractive index of the etalon.

The direct interaction between the optical beam and the cavity medium turned these devices specially attractive for optical sensing. Accordingly, Fabry-Pérot interferometers have been extensively used for sensing of physical and chemical parameters, by relying

on the measurement of the phase variations of the optical signal, reflected by or transmitted across the interferometer, induced by an alteration of the optical properties of the medium composing the cavity [131]. Most of the sensors so far reported are constructed on optical fibers, with multiple configurations having been demonstrated that can be further categorized in either intrinsic or extrinsic, depending if the cavity is located within a single fiber or if it is exterior to the optical fiber, respectively. For instance, examples of intrinsic fiber-based interferometers include the writing of two fiber Bragg gratings in the core of the optical fiber with the gratings operating as the cavity mirrors [132], or direct machining of the cavity at the core of the optical fiber either through laser ablation [133], fs-laser writing followed by chemical etching [134] or focused ion beam milling [135]. On the other hand, extrinsic interferometers have been fabricated by splicing a hollow capillary in between two single-mode fibers [136], or by depositing a partially reflective thin film on top of a cleaved fiber [137].

Meanwhile, only a few select papers discuss the fabrication of Fabry-Pérot interferometers in planar substrates with most of the reported devices consisting of hybrid systems. For example, Song *et al* [138] fabricated a three-dimensional microfluidic channel in a PMMA planar substrate for the purpose of flow generation and control, where the straight section of the channel was interrogated by an input and output single-mode fiber that were axially aligned and orthogonal to the sidewalls of the channel. The microfluidic channel operated as a Fabry-Pérot cavity, where the spectral shift induced by the presence/absence of cells within the volume intersecting the optical fiber was used to determine the refractive index and size of single living cells. To increase the mirror reflectivity, the end facets of the input and output optical fibers were coated with a layer of gold. With a similar configuration, Lin *et al* [139] constructed an interferometer in Foturan glass, comprised of a microfluidic channel fabricated through fs-laser direct writing followed by thermal annealing and chemical etching with HF acid, which was orthogonally intercepted by a single-mode fiber placed inside an ablated tunnel and ending near the channel. Operation of the device as a refractometer was successfully demonstrated. In both devices, the incompatibility shown by PMMA and Foturan glass in simultaneously fabricating optical waveguides and microfluidic channels meant that the optical layer consisted again of an optical fiber. However, in fused silica, optical waveguides can be written together with the microfluidic channel, which can be attractive as it provides a means for implementing several optical functions in a single substrate with the fluid handling capabilities being ensured by the microfluidic layer.

The motivation for this chapter is therefore to fabricate a monolithic Fabry-Pérot interferometer inside a fused silica substrate, as schematized in figure 5.1. A hollow microfluidic channel, operating as the Fabry-Pérot etalon, is fabricated at the surface of the fused silica substrate and is sealed by irreversibly bonding a PDMS cover layer to the substrate's surface. The PDMS layer also contains an inlet and outlet hole that can be connected to external tubings for injection or removal of the analyte from the microfluidic channel. An optical waveguide written orthogonally to the axis of the microfluidic channel and ending a few micrometers away from its closest sidewall is used to probe the

Fabry-Pérot cavity. Light coupled into the waveguide from an external single-mode fiber propagates forward and is launched into the cavity, with the reflected signal being coupled back into the waveguide before being measured in an optical detector. Given that the reflectivity of both cavity mirrors is inherently low as it is solely defined by the Fresnel reflection coefficients, the fabrication procedure has to be calibrated as the quality of the measured spectrum is quite sensitive to the insertion losses of the optical waveguide and to the geometrical and morphological characteristics of the microfluidic channel. Following this introduction, it is provided a theoretical background on the optical interference between waves propagating within the etalon and on the spectral properties of the output optical signal. It is then discussed the fabrication of the interferometer within a fused silica planar substrate, while examining how the design of the device and the fabrication parameters affect the signal-to-noise ratio and the finesse of the measured signal. From this calibration, a Fabry-Pérot interferometer is constructed and tested as a magnetic field sensor, with the detection of the magnitude of the magnetic field relying on the field-dependent refractive index property evidenced by a ferrofluid which is injected inside the microfluidic channel. In addition, it is also considered the role of the surface chemistry of the inner walls of the microfluidic channel in stabilizing the ferrofluid. Lastly, some final remarks summarizing the results obtained and regarding future improvements are made.

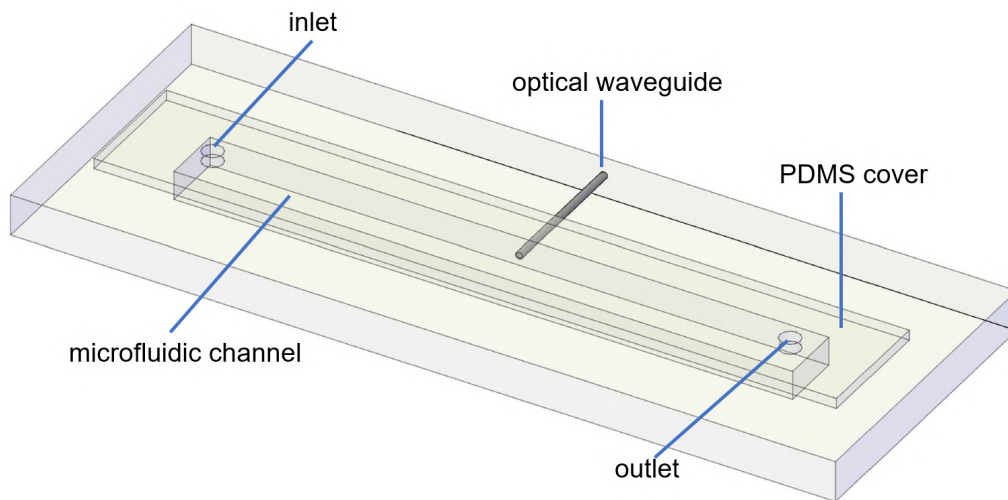


Figure 5.1: Design of the proposed Fabry-Pérot interferometer.

5.2 Fabrication of Fabry-Pérot Interferometers

5.2.1 Theoretical Background

According to figure 5.1, the Fabry-Pérot cavity consists of a microfluidic channel which is fabricated at the surface of the fused silica substrate and sealed with a PDMS cover layer containing openings for fluid delivery and withdrawal. A single optical waveguide, written orthogonal to the axis of the microfluidic channel and terminating a few micrometers from its closest sidewall, is used to simultaneously launch light

into the cavity and to collect the reflected signal. Given that the reflectivity at the fused silica – microfluidic channel interface is solely determined by Fresnel reflection, the analysis of the reflected signal can be simplified by considering that the device behaves as a low-finesse interferometer. Without any loss of information, the system can then be approximated by a two wave interferometer as shown in figure 5.2, with the intensity reflected by the Fabry-Pérot etalon at a specific wavelength ($I_r(\lambda)$) being defined by equation 5.1, where $I_1(\lambda)$ and $I_2(\lambda)$ are the intensities of the light beams travelling through paths 1 and 2 respectively, and δ is the phase difference between both waves. With the waveguide orthogonal to both interfaces of the interferometer, the phase difference δ is expressed by equation 5.2, where λ is the free-space wavelength, ΔL is the path difference between the two interfering waves corresponding to twice the cavity width, and n_{cavity} is the refractive index of the cavity/microfluidic channel. Note that equation 5.1 only expresses the signal reflected by the Fabry-Pérot interferometer and not the full measured signal, which also depends on the optical coupling coefficient from the interferometer back into the waveguide and on the insertion losses of the fs-laser written waveguide.

$$I_r(\lambda) = I_1(\lambda) + I_2(\lambda) + 2\sqrt{I_1(\lambda)I_2(\lambda)}\cos\delta \quad (5.1)$$

$$\delta = \frac{2\pi}{\lambda} \times \Delta L \times n_{cavity} \pm \pi \quad (5.2)$$

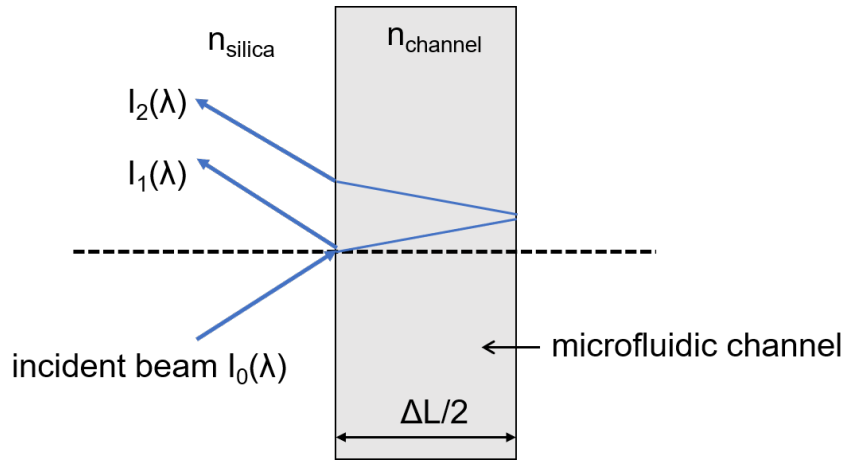


Figure 5.2: General configuration of the low-finesse Fabry-Pérot interferometer, where the reflected signal corresponds to the interference of two beams with intensities $I_1(\lambda)$ and $I_2(\lambda)$. The beam with intensity $I_1(\lambda)$ is reflected at the first fused silica – microfluidic channel interface (left), whereas the beam with intensity $I_2(\lambda)$ propagates across the microfluidic channel and is reflected at the second interface (right) before being transmitted across the first interface. The incident beam is designed at an oblique angle to facilitate visualization.

From equation 5.1, the output spectrum consists of a sinusoidal signal composed by resonant peaks (λ_m) located at the wavelengths for constructive interference between the interfering beams (*i.e.* resonances occur when δ is a multiple of 2π) as defined in equation 5.3 where m is an integer. Consecutive peaks (λ_m, λ_{m+1}) are periodically spaced by the free spectral range ($\Delta\lambda$) which can be defined by equation 5.4. The

spectral properties of the reflected signal can be quantified through the fringe visibility (V) and finesse coefficient (F) expressed in equations 5.5 and 5.6, respectively, where R_{FP} is the total reflected power. In optical sensing, both of these quantities should be maximized as it provides a higher measurement resolution and a higher limit of detection.

$$\lambda_m = \frac{n_{cavity} \times \Delta L}{m} \quad (5.3)$$

$$\Delta\lambda = \frac{\lambda_m \lambda_{m+1}}{n_{cavity} \times \Delta L} \quad (5.4)$$

$$V = \frac{I_{max} - I_{min}}{I_{max} + I_{min}} = \frac{2\sqrt{I_1 I_2}}{I_1 + I_2} \in [0, 1] \quad (5.5)$$

$$F = \frac{4R_{FP}}{(1 - R_{FP})^2} \quad (5.6)$$

Equation 5.3 also reveals that the resonant wavelength shifts in response to variations in the refractive index or in the width of the etalon, thereby demonstrating the working principle for optical sensing. The sensitivity (S) to refractive index variations can be expressed through equation 5.7, from which it is concluded that the sensitivity increases whenever: (i) the path difference, and consequently the cavity width, increases for a constant integer m , or (ii) when measuring at higher wavelengths where the integer m is smaller.

$$S = \frac{\Delta\lambda}{\Delta n} = \frac{\Delta L}{m} \quad (5.7)$$

5.2.2 Fabrication of the Device and Calibration of the Design Parameters

The fabrication of the device depicted in figure 5.1 starts with fs-laser direct writing following the irradiation pattern shown in figure 5.3. First, it is written the optical waveguide by scanning the substrate across the focus of the fs-laser beam along the +X direction, *i.e.* scanned from the facet of the substrate inwards. Then, the microfluidic channel is written, whose irradiation path is obtained by slicing the volume of the microfluidic channel into several planar layers spaced along Z by 5 μm , which are further hatched into multiple laser-exposure tracks uniformly separated by 3 μm along X. Each laser-exposure track is irradiated with a 60 nJ pulse energy and scanned at a velocity of 3000 $\mu\text{m/s}$ by translating the substrate in relation to the focus of the fs-laser beam along +Y, with the tracks being orderly scanned along the +X direction (*i.e.* from left to right) and along -Z (*i.e.* from the bottom of the microfluidic channel towards the surface of the substrate). The optical waveguide ends at a user-defined distance from the closest interface of the cavity. Further, by writing the waveguide and microfluidic channel simultaneously, it is guaranteed perfect alignment and orthogonality between both. In all situations, the optical waveguide is written with the laser beam polarized parallel to the scanning direction, while the laser-exposure tracks defining the microfluidic channel are written with the laser beam polarized orthogonally to the scanning direction.

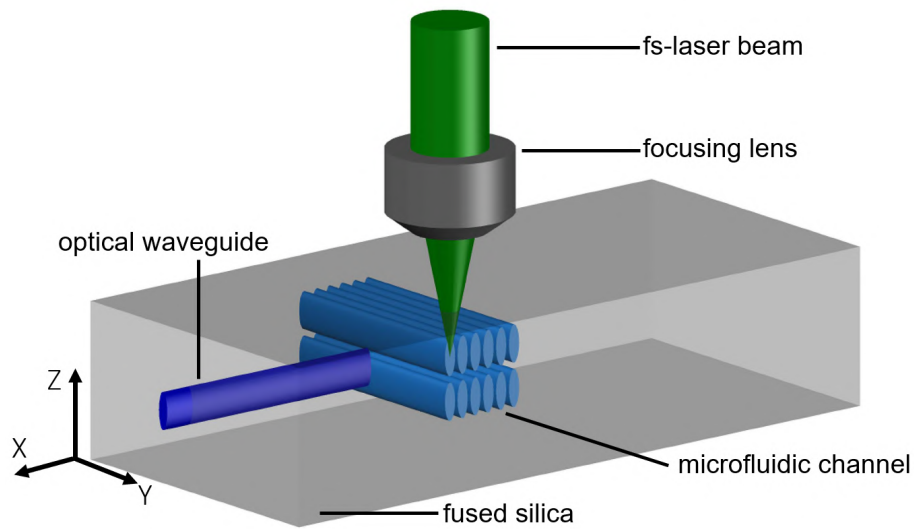


Figure 5.3: Laser-irradiation path for direct writing of the Fabry-Pérot interferometer.

After fs-laser direct writing, the substrate is etched in an ultrasonic cleaner containing an HF acid solution with a volume concentration of 10%, following the procedure outlined in section 3.1.2. The etching reaction is stopped when the bottom of the microfluidic channel reveals a profile similar to the one shown in figure 5.4(a), where the entire laser-irradiated volume has been removed and the inner sidewalls of the microfluidic channel are smooth as can also be observed in the cross-section image in figure 5.4(c). Due to the limited etching selectivity, the HF acid also attacks the pristine material surrounding the microfluidic channel which causes the size of the cavity to increase past the designed dimensions and the gap between the end of the optical waveguide and the closest sidewall of the microfluidic channel to decrease from the assigned value. Accordingly, to avoid the etchant from penetrating through the waveguide, the device is designed with an initial gap of at least 5 μm . Nevertheless, because the HF acid corrodes the entrance of the optical waveguide at the substrate edges, it is necessary to mechanically polish the entrance facet of the substrate after chemical etching.

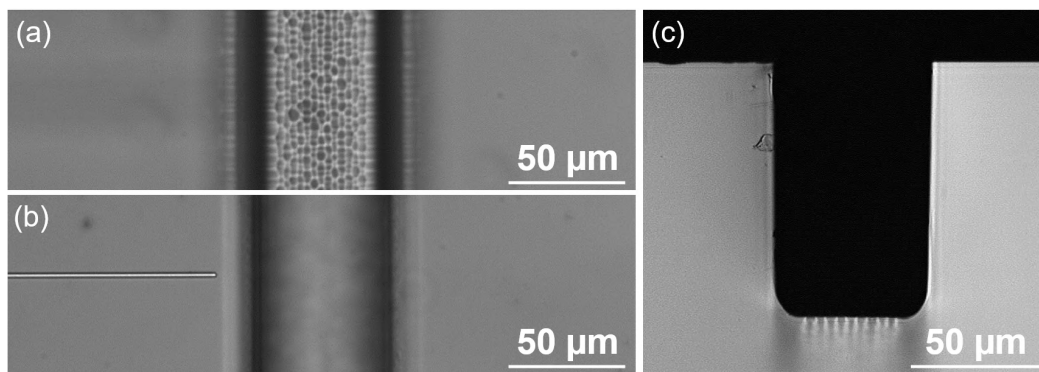


Figure 5.4: Top view images of the device after chemical etching focused (a) at the bottom of the microfluidic channel and (b) at the fs-laser written waveguide. (c) Cross-section image of the microfluidic channel obtained after chemical etching and by polishing the substrate until the channel is at the facet of the substrate.

Further, with this writing configuration, the minimum achievable width of the microfluidic channel is limited by the width of a single laser-exposure track, which corresponds to 2 μm for the chosen exposure parameters, and by the limited etching selectivity which increases the width of the cavity during chemical etching at a rate of 0.2 $\mu\text{m}/\text{min}$ (twice the etch rate of the pristine medium).

Imperfections in the quality of the interface, either due to the surface roughness or due to tilted or curved surfaces, can decrease the finesse of the interferometer [140, 141]. Accordingly, it is necessary to discuss the influence of the fabrication parameters of the microfluidic channel on the quality of the reflected signal. First, the roughness of the sidewalls of the microfluidic channels is mainly defined by the vertical spacing between laser-exposure tracks. Keeping in mind that the height of a single laser-exposure track is 10 μm (at a pulse energy of 60 nJ and scanning speed of 3000 $\mu\text{m}/\text{s}$ with the fs-laser beam polarized parallel to the scanning direction), it is observed that the defined vertical spacing of 5 μm ensures a good overlap along Z between laser-exposure tracks which minimizes the surface roughness. An evaluation of the cross-section of the microfluidic channel after chemical etching, shown in figure 5.4(c), already points to a smooth and uniform sidewall, with its surface roughness estimated to be around tens of nanometres (as will be explained in more detail in section 6.3.1) [130]. Further, to avoid the incident light beam from being reflected/refracted at a variable and oblique angle due to the curved sidewall present at the bottom of the microfluidic channel, the optical waveguide is written beneath the surface of the substrate at a depth half of the depth of the microfluidic channel. From figure 5.4(c), it is also observed that the sidewalls of the microfluidic channel are tilted from the vertical direction by 0.4° , which means that the interfaces can be considered parallel to each other and that light propagating through the optical waveguide is launched into the cavity at normal incidence. Therefore, the chosen fabrication parameters of the microfluidic channel minimize imperfections in the cavity mirrors that would otherwise contribute to a poor finesse.

Still, the spectral quality of the measured signal is influenced by other parameters. To assess how the insertion losses and loss mechanisms of the fs-laser written waveguides affect the measured signal, three 1 cm long microfluidic channels with a rectangular cross-section of 18/37/58 μm by 105 μm (width by height) were fabricated at the surface of a fused silica substrate, with several 1.25 cm long waveguides, written 55 μm beneath the substrate's surface and transversally separated by 100 μm to prevent optical coupling between each other, probing each Fabry-Pérot etalon. Each waveguide was written with a specific pulse energy and translation velocity, ranging from 75 nJ to 250 nJ and from 25 $\mu\text{m}/\text{s}$ to 3200 $\mu\text{m}/\text{s}$, respectively. All waveguides terminated 20 ± 1 μm from the closest sidewall of the microfluidic channel. To characterize the device, the reflected spectrum was measured according to the protocol established in section 3.2.3 and with the measurement setup of figure 3.10. A broadband source EXFO Optical System IQ-203 with an integrated ASE source module IQ-2300 and an optical spectrum analyser Yokogawa AQ3670D served as optical source and detector, respectively. The measurements were carried from 1500 nm to 1600 nm with a resolution of 1 nm at a

temperature of 20°C, with the obtained spectra being normalized to the transmission spectrum of the optical source. Also, all spectra are represented in a normalized linear scale. The optical characterization was also repeated for different refractive indices of the cavity, having been tested the following fluids: air, Cargille Series AAA oil-based fluids $n_D^{25^\circ\text{C}} = 1.3100$ and $n_D^{25^\circ\text{C}} = 1.3900$. All fluids display negligible absorption within the measurement range and for the cavity widths tested, with the respective Cauchy or Sellmeier coefficients being mentioned in annex A. The fluids were drawn into each microfluidic channel through capillarity, having been confirmed that no air bubbles formed inside the cavity. In between measurements, the sample was thoroughly cleaned to avoid cross-contamination.

The spectra gathered for an 18 μm wide empty microfluidic channel (*i.e.* refractive index of the cavity equal to 1.0003 at 1550 nm) is shown in figure 5.5(a-c) for probing optical waveguides written with different pulse energies and scanning velocities. Regardless of the writing parameters of the optical waveguide, the measured signal reveals an oscillatory pattern with a period of 70 nm which is consistent with the expected free spectral range given by equation 5.4 (around 67 nm). Further, it was also confirmed that the free spectral range decreases with $\frac{1}{n_{\text{cavity}} \times \Delta L}$ as the refractive index (n_{cavity}) and/or the width (ΔL) of the Fabry-Pérot cavity increased. Still, two distinct features, seemingly independent from the width and refractive index of the cavity, are observed: (i) the amplitude of the oscillatory signal depends on the pulse energy and scanning velocity used to fabricate the optical waveguide, and (ii) the measured signal also contains a random high-frequency modulation.

Regarding the first observation, the amplitude of the oscillatory pattern is related to the finesse of the interferometer. From figure 5.5(a-c), it is observed that this amplitude, and consequently the finesse, decrease monotonically with the scanning speed for waveguides written with a pulse energy of 75 nJ. In particular, no oscillatory pattern is visible for translation velocities of 1600 $\mu\text{m/s}$ and 3200 $\mu\text{m/s}$. For the waveguides written with a pulse energy of 100 nJ or higher, the amplitude (and finesse) start to increase with the translation velocity until a speed of 200-400 $\mu\text{m/s}$, and decreases thereafter. Meanwhile, for waveguides written with a translation velocity of 800 $\mu\text{m/s}$ or higher, the amplitude (and finesse) increase with the pulse energy. Further, this behaviour is also observed for the 36 μm and 57 μm wide cavities and when filling the cavity with liquids of higher refractive index, which confirms that it depends on the writing parameters of the optical waveguide and not on the optical interference condition nor on the dimensions of the microfluidic channel. Accordingly, to understand these results, in figure 5.5(d-f) it is also represented the insertion losses of similarly designed 2.5 cm long optical waveguides with the transmission spectrum measured according to the procedure outlined in section 3.2.3 (the optical source and optical detector and the measurement span and resolution used were the same ones to characterize the Fabry-Pérot interferometers).

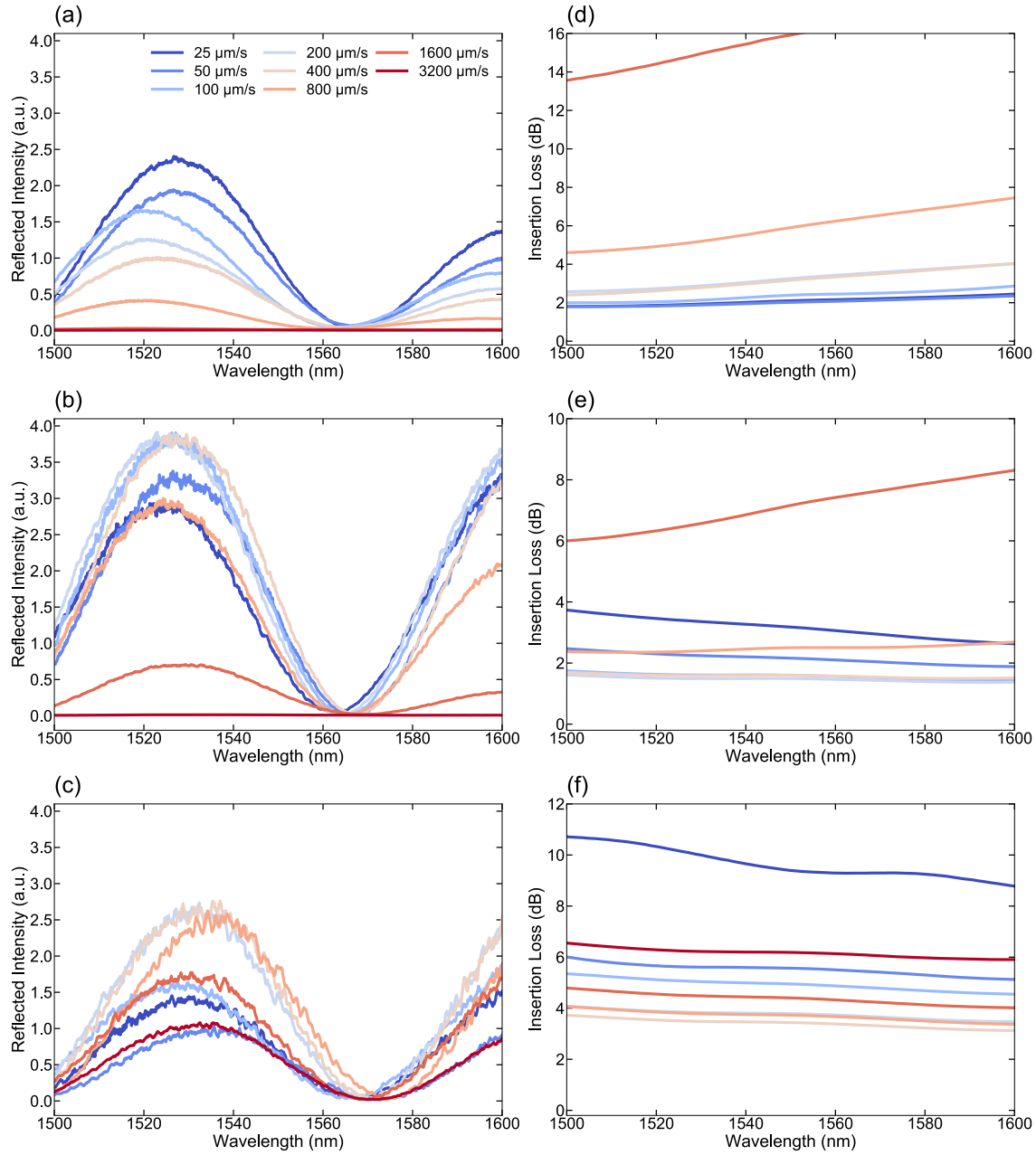


Figure 5.5: (a-c) Measured reflected spectra of an 18 μm wide empty microfluidic channel intercepted by optical waveguides written with variable pulse energy and translation velocity, and (d-f) insertion loss profile of the correspondent 2.5 cm long fs-laser writing waveguides. The reflected spectra are represented in linear scale to facilitate the analysis. Figures (a-d) correspond to waveguides written with a pulse energy of 75 nJ, (b-e) with 100 nJ, and (c-f) with 200 nJ.

After analysing figure 5.5, it can be confirmed that the insertion losses of fs-laser written waveguides vary with the writing parameters in a similar fashion to the behaviour displayed by the amplitude of the interferometric signal. In particular, a larger amplitude of the measured reflected signal is obtained if the insertion losses of the fs-laser written waveguide are reduced. Therefore, in order to maximize the finesse, the insertion losses of the optical waveguide should be kept at a minimum. Note that equation 5.6 does not explicitly show how the finesse depends on the optical losses of the fs-laser written

waveguide. However, it can be easily understood that a waveguide exhibiting high coupling and/or propagation losses leads to a decrease in the optical power of the light beam launched into the cavity and to a decrease in the power coupled from the waveguide back into the lead-in/lead-out optical fiber, which translates into a lower amplitude of the measured interference signal and, consequently, to a lower fringe contrast and finesse.

Figure 5.5(a-c) also shows that the measured signal contains a random high-frequency modulation. This modulation is more easily seen in the spectra corresponding to optical waveguides written at higher pulse energies, and was confirmed for all widths and refractive indices of the Fabry-Pérot cavity tested. Based on these observations it is again expected that the high-frequency modulation is caused by the loss mechanisms of the fs-laser written waveguide. To understand this phenomenon, the signal-to-noise ratio (SNR) of each spectrum was calculated according to equation 5.8, where $\text{RMS}_{\text{signal}}$ and $\text{RMS}_{\text{noise}}$ are the root-mean square of the measured signal and of the respective noise component, respectively. The noise component was computed by applying a band-pass filter to the measured signal in order to remove the spectral components associated to the optical interference, *i.e.* the noise term is estimated by filtering out the spectral components with period centred around the measured free spectral range. Figure 5.6 shows the measured spectrum for an optical waveguide written with a pulse energy and translation velocity of (a) 75 nJ and 25 $\mu\text{m/s}$ and (b) 150 nJ and 25 $\mu\text{m/s}$, respectively, as measured and after application of the filter, to demonstrate how the noise component was obtained.

$$\text{SNR} = 20 \times \log_{10} \left(\frac{\text{RMS}_{\text{signal}}}{\text{RMS}_{\text{noise}}} \right) \quad (5.8)$$

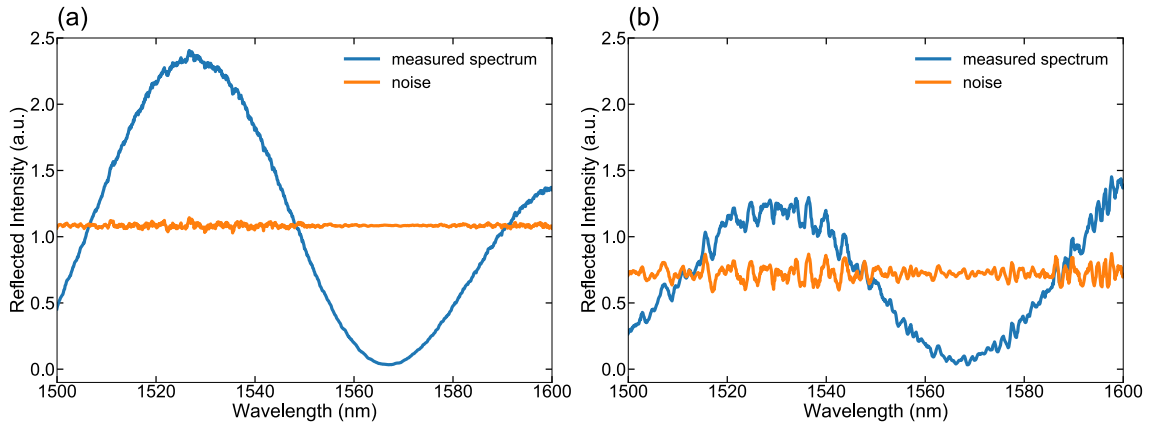


Figure 5.6: Measured spectrum and computed noise component of an 18 μm wide empty microfluidic channel intercepted transversally by an optical waveguide written with a pulse energy and translation velocity of (a) 75 nJ and 25 $\mu\text{m/s}$ and (b) 150 nJ and 25 $\mu\text{m/s}$, respectively.

The calculated SNR are plotted in figure 5.7(b-d) against the pulse energy and scanning speed used to write the optical waveguide. No values are reported for some writing conditions due to a very weak fringe contrast which prevents an accurate separation of the interferometric signal from the noise component. For all translation

velocities tested, it is observed that the SNR decreases as the pulse energy increases, similarly to what can be qualitatively concluded by analysing figures 5.5(a-c) and 5.6. The SNR map also shows that, in general, for pulse energies lower than 150 nJ the SNR barely varies with the translation velocity for scanning speeds between 25 $\mu\text{m/s}$ and 800 $\mu\text{m/s}$. Further, this behaviour is common for all cavity refractive indices tested.

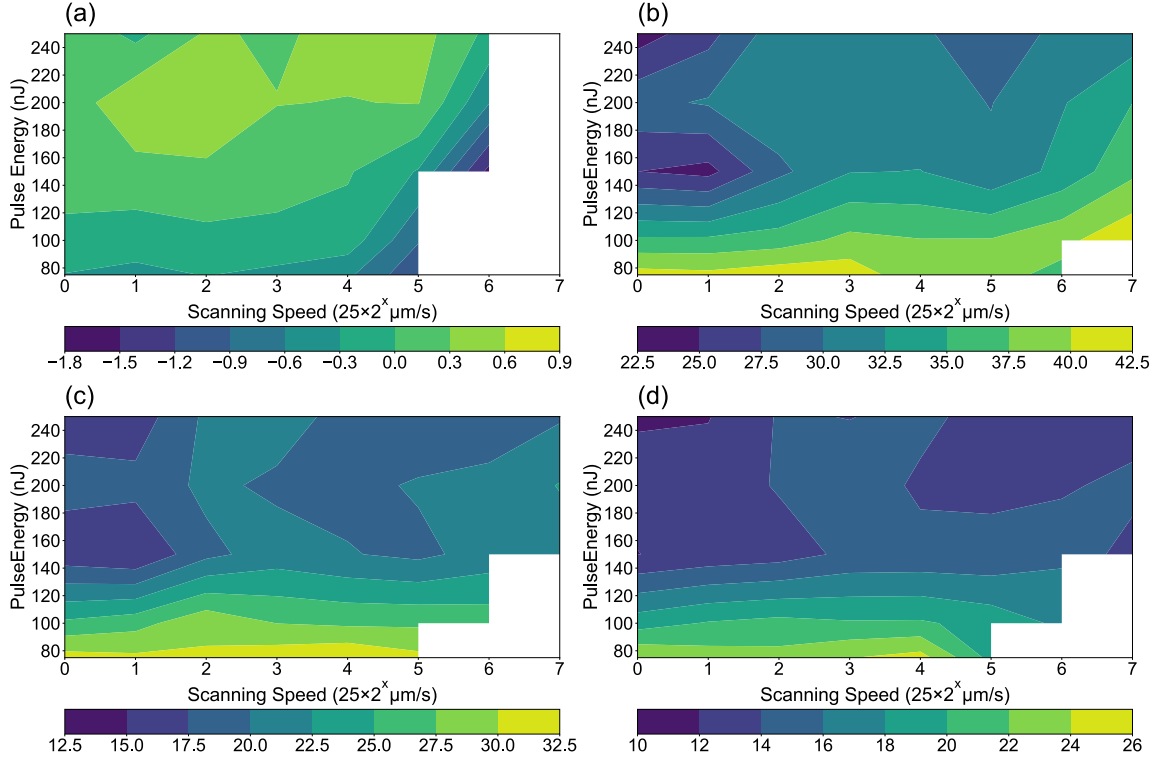


Figure 5.7: (a) Mie scattering coefficient (in dB/cm) of fs-laser written optical waveguides fabricated with pulse energy and translation velocity ranging from 75 nJ to 250 nJ and 25 $\mu\text{m/s}$ to 1600 $\mu\text{m/s}$, respectively. (b-d) Signal-to-noise ratio (dimensionless) of an 18 μm wide microfluidic channel against the pulse energy and translation velocity used to write the optical waveguide, with the fluid within the cavity corresponding to (b) air, (c) Cargille Series AAA oil-based liquid $n_D^{25^\circ\text{C}} = 1.3100$, and (d) Cargille Series AAA oil-based liquid $n_D^{25^\circ\text{C}} = 1.3900$.

To comprehend these results, the work developed by Amorim *et al* [5] should be revisited, which focused on the loss mechanisms of fs-laser written waveguides. There, the propagation losses of the optical waveguides depended on Rayleigh and on Mie scattering. Rayleigh scattering is caused by inhomogeneities present in the waveguide that are smaller than the wavelength of the propagating beam, with the scattering coefficient increasing with the translation velocity while revealing a complex dependence on the pulse energy. Meanwhile, Mie scattering is attributed to defects within the waveguide with a dimension similar to the wavelength of the propagating beam. The respective scattering coefficient was found to be independent of the wavelength and to increase with the pulse energy, while being independent of the translation velocity for

speeds lower than 1600 $\mu\text{m/s}$ and decreasing as the translation velocity grows from 1600 $\mu\text{m/s}$ onwards.

To understand if any of these scattering mechanisms is related to the high-frequency modulation observed in figure 5.5(a-c), several optical waveguides were written with lengths of 1.2, 2.2 and 3.2 ± 0.1 cm with pulse energy and translation velocity ranging from 75 nJ to 250 nJ and 25 $\mu\text{m/s}$ to 3200 $\mu\text{m/s}$, and their insertion losses were measured according to the procedure outlined in section 3.2.3. The spectra were measured from 350 nm to 1750 nm with a resolution of 10 nm with an halogen lamp as optical source and with an optical spectrum analyser ANDO AQ-6315B as optical detector; the retrieved spectra were normalized to the transmission spectrum of the radiation source. Given that within the measurement range, the absorption of fused silica is null and that Fresnel losses at the coupling fiber – substrate interface are null, the insertion losses (IL) of an optical waveguide at wavelength λ are defined by $IL(\lambda) = 2CL(\lambda) + PL(\lambda) \times L$, where CL is the coupling loss, PL the propagation loss and L the length of the waveguide. Accordingly, by fabricating waveguides with different length, the cut-back technique can be used to separate the coupling losses from the propagation losses by fitting the retrieved spectra with a linear regression for each wavelength. With the propagation losses depending on optical losses due to Rayleigh and Mie scattering, the respective coefficients were obtained by fitting the propagation loss curve with the following expression $PL = \frac{C_{RS}}{\lambda^4} + C_{MS}$, where C_{RS} and C_{MS} are the Rayleigh and Mie scattering coefficients, respectively.

The map obtained for the Mie scattering coefficient is represented in figure 5.7(a), where some data points are missing due to the high optical losses of the respective waveguide which prevent an accurate fitting. At the same time, the negative coefficient verified for waveguides written with pulse energy of 75 nJ and translation velocity of 1600 $\mu\text{m/s}$ or higher is unrealistic and is attributed to a poor fit caused by the lack of a nearly constant spectral component at higher wavelengths and to the rapidly varying propagation loss data.

Comparing the Mie scattering coefficient of figure 5.7(a) with the measured SNR of the Fabry-Pérot interferometers of figures 5.7(b-d), the evolution of the SNR with the writing parameters of the optical waveguide is similar to the behaviour displayed by the Mie scattering coefficient. Therefore, micrometre-sized defects formed within the waveguide during laser direct writing that provoke Mie scattering are also responsible for the noise component in the reflected spectrum of the Fabry-Pérot interferometer. These inhomogeneities formed within the optical waveguide cause random reflections that manifest as arbitrary interferometers, which also explain the random nature of the high-frequency modulation.

In addition, figure 5.8 shows top view images of fs-laser written optical waveguides fabricated at different pulse energies and with a translation velocity of 100 $\mu\text{m/s}$ (left) and 400 $\mu\text{m/s}$ (right), from which it is observed that the waveguide becomes more rugged as the pulse energy increases regardless of the translation velocity. These defects could also explain why the Mie scattering coefficient is higher as the pulse energy increases. Also, the behaviour of the Rayleigh scattering coefficient against the waveguide writing

parameters did not mimic the evolution of the SNR, showing that this effect is unrelated to the high-frequency modulation observed in the reflected spectrum of the interferometer.

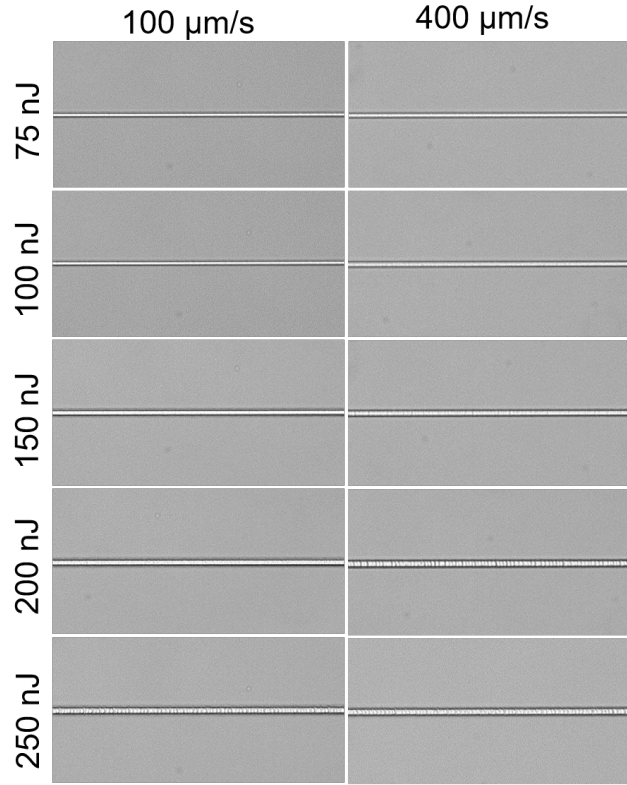


Figure 5.8: Top view image of fs-laser written waveguides with a translation velocity of 100 $\mu\text{m/s}$ (left column) and 400 $\mu\text{m/s}$ (right column) against pulse energy.

The behaviour evidenced in figure 5.7(b-d) was also observed when analysing the spectra obtained for other widths and refractive indices of the cavity, where, nevertheless, the maximum SNR was seen to decrease as the refractive index of the cavity increased. In particular, the SNR of a 18 μm wide cavity, which was found maximum for an optical waveguide written at 75 nJ and 25 $\mu\text{m/s}$, decreased from 42.5 to 32.5 to 24 when the refractive index (at 1550 nm) increased from 1.0003 to 1.306 to 1.383, respectively. For a low-finesse interferometer, the reflectivity (R) of each interface can be obtained from the Fresnel reflection coefficient (r_{Fresnel}), which for normal incidence can be expressed through equation 5.9. According to this equation, as the refractive index contrast between both mediums decreases, which corresponds to increasing the refractive index of the cavity, the reflectivity of each mirror decreases. In turn, the SNR reduction is caused by the decrease in the intensity of the reflected signal from the interferometer, and not by an increase in the RMS value of the noise component.

$$R = (r_{\text{Fresnel}})^2 = \left| \frac{n_{\text{cavity}} - n_{\text{silica}}}{n_{\text{cavity}} + n_{\text{silica}}} \right|^2 \quad (5.9)$$

It can then be concluded that the writing parameters of the optical waveguide significantly affect the spectral properties of the reflected signal from the Fabry-Pérot interferometer. The insertion losses of the fs-laser written waveguide should be minimum

to improve the finesse (and measurement resolution), while the Mie scattering coefficient should be reduced to maximize the SNR. Both conditions cannot be met simultaneously, which result in a compromise between maximizing the SNR or the finesse. In the ensuing tests, the optical waveguide probing the Fabry-Pérot cavity was written with a pulse energy of 75 nJ and a translation velocity of 25 $\mu\text{m/s}$ to maximize the SNR. Although the insertion losses of the fs-laser written waveguide sit around 2 dB at 1550 nm, even lower losses of 1.5 dB could be obtained with an optical waveguide written at 100 nJ and 400 $\mu\text{m/s}$. Further, note that neither of the issues are encountered in configurations where an optical fiber probes the etalon, due to their extremely low attenuation losses at 1550 nm and due to the inexistence of defects and/or refractive index inhomogeneities which could otherwise cause optical scattering.

In a second test, it was considered the influence of the distance from the end of the optical waveguide to the closest interface of the cavity on the spectral properties of the measured signal. Three 3.55 mm long microfluidic channels with a rectangular cross-section with dimensions of 24/45/64 μm by 100 μm (width by height), respectively, were fabricated at the surface of a fused silica substrate. Several 1.35 cm long waveguides orthogonally intercepting each microfluidic channel were written and ended at a specific distance, ranging from 5 μm to 995 μm , from the closest channel sidewall. Again, each waveguide is transversally distanced by 100 μm to avoid optical coupling between each. The optical waveguide and microfluidic channel were fabricated with the optimal exposure parameters mentioned previously. All interferometers were characterized following the same procedure described earlier in this chapter, and for different fluids within the cavity: air, Cargille Series AAA oil-based fluids $n_D^{25^\circ\text{C}} = 1.3100$ and $n_D^{25^\circ\text{C}} = 1.3900$. The reflected spectra obtained for the empty 45 μm wide cavity are shown in figure 5.9. The gathered spectra shows that the amplitude of the sinusoidal modulation monotonically decreases as the the distance between the end of the waveguide and the microfluidic channel increases; this behaviour was also observed for the wider Fabry-Pérot interferometers and for the other liquids within the cavity. This phenomenon is related to divergence of the optical beam propagating within the pristine layer separating the optical waveguide from the microfluidic channel. Assuming a Gaussian profile at the output of the fs-laser written waveguide, the size of the beam increases by $\sqrt{1 + \frac{z}{z_r}}$ where z is the distance from the end of the waveguide and z_r is the Rayleigh range which defines the distance at which the beam radius increases by $\sqrt{2}$ from its initial value. Here, the size of the beam incident on the etalon progressively increases as the distance between both structures increases. Similarly, the beam reflected by the Fabry-Pérot cavity further diverges when propagating through the pristine layer in direction to the optical waveguide. Consequently, as the dimensions of the reflected beam gradually increase due to the higher separation between the waveguide and the microfluidic channel, the optical beam starts to fall outside the waveguide's acceptance angle, resulting in a lower recoupling of light back into the optical waveguide and, in turn, to a lower amplitude of the measured oscillatory signal and lower finesse. The behaviour shown in figure 5.9 is then attributed to optical divergence of the beam propagating within

the pristine layer, which is more significant the wider the gap between the fs-laser written waveguide and the Fabry-Pérot cavity. It is also expected for the dimensions of the beam to not increase linearly with this gap, but to rather follow a $\sqrt{1 + \frac{z}{z_r}}$ trend. This also explains why the amplitude of the oscillatory signal barely varies for gaps lower than 20 μm , and why it starts to decrease more rapidly from there onwards. Although these results mean that the waveguide should be fabricated as close as possible to the microfluidic channel, they also indicate that there is a buffer of around 15-20 μm in which the finesse is almost constant. This buffer provides some flexibility in the designed distance between both structures, which minimizes the risk of the HF acid etching through the waveguide and, in turn, of damaging the device.

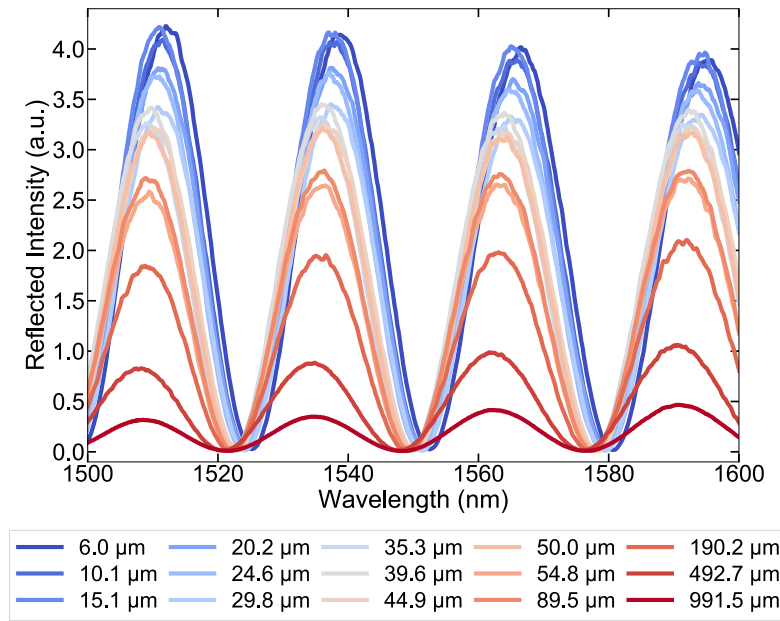


Figure 5.9: Measured reflected spectrum of a 45 μm wide empty microfluidic channel orthogonally intercepted by an optical waveguide written with a pulse energy of 75 nJ and translation velocity of 25 $\mu\text{m}/\text{s}$, against several distances between the end of the fs-laser written waveguide and the closest interface of the etalon.

5.2.3 Refractive Index Sensing

Having calibrated the writing parameters of the optical waveguide and of the microfluidic channel, it is discussed the potential of planar Fabry-Pérot interferometers as refractometers. To that effect, a $400 \times 36 \times 110 \mu\text{m}^3$ microfluidic channel (length $\times$ width $\times$ depth) was fabricated at the surface of a fused silica substrate using the previously mentioned exposure parameters that minimized the surface roughness of the cavity mirrors. A 1.3 cm long optical waveguide, orthogonally intercepting the microfluidic channel and ending $9 \pm 1 \mu\text{m}$ from the closest interface, was written 65 μm beneath the substrate's surface with a pulse energy of 75 nJ and a translation velocity of 25 $\mu\text{m}/\text{s}$, and with the laser beam polarized parallel to the scanning direction. As just discussed, these parameters provide a high SNR and finesse by minimizing the Mie scattering coefficient and by providing low insertion losses, respectively. The device was characterized against

the refractive index of the cavity by measuring the reflected spectrum (similar procedure to the one described earlier in the chapter) for different Cargille Series AA and AAA oil-based liquids inside the cavity: $n_D^{25^\circ\text{C}} = 1.3000$, $n_D^{25^\circ\text{C}} = 1.3200$, $n_D^{25^\circ\text{C}} = 1.3400$, $n_D^{25^\circ\text{C}} = 1.3600$, $n_D^{25^\circ\text{C}} = 1.3800$, $n_D^{25^\circ\text{C}} = 1.4000$, $n_D^{25^\circ\text{C}} = 1.4200$. All fluids display negligible absorption around 1550 nm, with the respective Sellmeier or Cauchy coefficients being mentioned in annex A. The fluids were drawn into the microfluidic channel through capillarity, having been confirmed that no air bubbles formed inside the cavity. In between measurements, the sample was thoroughly cleaned to avoid cross-contamination. The measurements were carried at a temperature of $18 \pm 1^\circ\text{C}$. The obtained results are represented in figure 5.10(a), where it is observed that the resonant wavelengths shift with the refractive index of the cavity, and that the amplitude of the measured oscillatory signal decreases as the refractive index of the cavity increases.

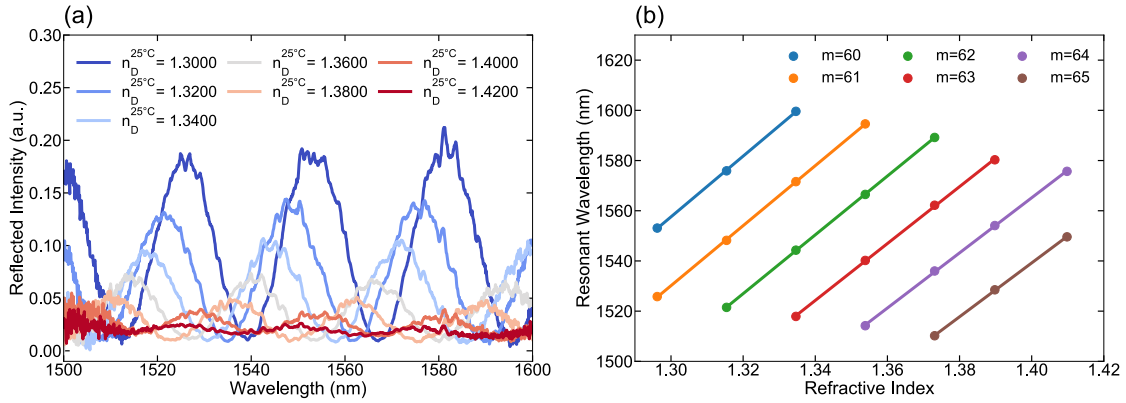


Figure 5.10: (a) Measured reflected spectrum of a 36 μm wide microfluidic channel orthogonally intercepted by an optical waveguide written with a pulse energy of 75 nJ and translation velocity of 25 $\mu\text{m/s}$, against the refractive index of the cavity. (b) Evolution of the resonant wavelength against the refractive index of the etalon. The refractive index mentioned in the x-scale of both plots corresponds to the refractive index of the used Cargille liquids at 1550 nm.

First, to understand how the resonant wavelength shifts with the refractive index of the etalon, the peak wavelengths of each spectrum are computed and grouped by the respective parameter m according to equation 5.3. The results are summarized in figure 5.10(b), where it is observed that the resonant wavelength, for a specific m , increases linearly with the refractive index of the cavity, as expected from equation 5.3. Each curve is then fitted with a linear regression in order to estimate the sensitivity of the interferometer to variations of the refractive index, with the obtained values being reported in table 5.1. In all cases, a regression coefficient higher than 0.9999 is obtained proving the good linearity between the measured data. In particular, a maximum sensitivity of 120 ± 13 nm/RIU is measured for a refractive index ranging from 1.296 to 1.410 (refractive indices at 1550 nm) and for a parameter $m = 60$. According to table 5.1, the sensitivity (S) also decreases with the parameter m as expected from the theoretical equation 5.7 which is repeated here for clarity $S = \frac{\Delta L}{m}$. The expected sensitivity can also be calculated from this equation, from which it is concluded that the measured sensitivity

is always within 3% of the theoretical value. This slight variation is attributed to the $\pm 1 \mu\text{m}$ error associated to the measurement of the cavity width.

m	sensitivity (nm/RIU)	error (nm/RIU)	uncertainty
60	1209	13	0.9%
61	1195	7	1.4%
62	1172	4	1.0%
63	1134	11	0.6%
64	1098	10	2.3%
65	1073	14	3.1%

Table 5.1: Summary of the measured sensitivities against variations in the refractive index of the cavity for different integers m (corresponding to different resonances of the interferometer) with the respective measurement error and uncertainty from the theoretical value.

In addition, according to equation 5.9, the Fresnel reflection coefficient, which defines the reflectivity of both mirrors, decreases as the refractive index contrast between the pristine medium and cavity lowers. Accordingly, as the reflectivity of the interferometer decreases, the measured intensity of the reflected signal measured is also reduced, which explains the behaviour shown in figure 5.10(a) where the amplitude of the oscillatory signal lowers as the refractive index of the cavity increases. This reduction in the reflectivity of the Fabry-Pérot interferometer also translates into a lower signal-to-noise ratio and finesse, which limit the operation range of the sensor and the measurement resolution. Here, the use of the device as a refractometer is limited to the liquid Cargille $n_D^{25^\circ\text{C}} = 1.4200$, corresponding to a refractive index of 1.410 (at 1550 nm). The measurement range can be enlarged and the resolution (and limit of detection) can be improved by increasing the reflectivity of both interfaces. For planar-based substrates, Simoni *et al* [142] increased the reflectivity of each mirror to 60-95% by fabricating a thin hollow cavity between the lead-in/lead-out probing optical fibers and each sidewall of the microfluidic channel, followed by filling it with a silver organic complex ink which sintered into a silver film through thermal treatment. Liquids with high optical absorption also limit the operation range of the sensor.

Although not discussed here, the fringe visibility also decreases as the cavity widens [143]. This effect can be understood from equation 5.5, where the intensity $I_1(\lambda)$ of the beam travelling through path 1 (*i.e.* beam reflected by the closest interface) is independent from the width of the cavity, whereas the intensity $I_2(\lambda)$ of the beam travelling through path 2 (*i.e.* beam transmitted through the cavity and reflected from the farther interface) depends on the width of the cavity. By increasing the width of the cavity, the size of the beam propagating through path 2 enlarges due to optical divergence (as discussed earlier) which causes the respective reflected beam to fall outside the waveguide's acceptance angle, resulting in a lower recoupling of light back into the optical waveguide and in a lower intensity $I_2(\lambda)$. In turn, the ratio between the intensities $I_2(\lambda)$ and $I_1(\lambda)$ decreases as the cavity widens, which lowers the fringe visibility and the finesse. It has been demonstrated that in order to have optimal finesse

in low-finesse interferometers, and consequently a better measurement resolution, the cavity width should not be higher than 50 μm [143]. Zhang *et al* [143] were also able to increase the fringe visibility of an extrinsic fiber-based Fabry-Pérot interferometer formed by two longitudinally separated but axially aligned single-mode fibers, by fusion splicing a quarter-pitch length graded-index fiber to the cleaved facet of the lead-in single mode fiber.

5.3 Magnetic Field Sensing

Optical-based sensors have been proposed as an alternative to electrical-based sensors for magnetic field detection due to the potential for remote operation and multiplexing and due to the low cost and smaller dimensions of the devices (specially when compared to typical SQUID magnetometers). To overcome the low sensitivity exhibited by fused silica to magneto-optical effects (*e.g.* Faraday rotation and magneto-optic Kerr effect), these sensors are typically combined with active materials, in particular with ferrofluids or magnetic fluids, whose optical properties change under an external magnetic field [144, 145]. These fluids consist of stable colloidal suspensions of single-domain magnetic nanoparticles, usually magnetite (Fe_3O_4) or iron dioxide (Fe_3O_2) nanoparticles with average diameter of 5-10 nm, dispersed in an aqueous or non-polar solvent, such as hydrocarbons or liquid metals. The distribution of the nanoparticles within the carrier liquid is shown in figure 5.11. If no magnetic field is applied, the nanoparticles are randomly distributed in the carrier liquid and the medium can be considered optically isotropic. When subjected to an external magnetic field, if the magnitude of the field is enough to overcome Brownian and diffusive forces, the nanoparticles start to interact with each other and their magnetic moment becomes aligned with the direction of the applied field due to Brownian rotational diffusion (rotation of the nanoparticles) and/or Néel relaxation (rotation of the magnetic moment within the nanoparticle) [146, 147]. These interactions lead to the formation of magnetic columns aligned with the direction of the external field, who grow in number and size as the magnitude of the magnetic field increases until a saturation state is reached [148]. According to figure 5.11(b), under an external field the nanoparticles are distributed anisotropically within the carrier liquid. Removing the external field causes the nanoparticles to re-disperse in the carrier liquid due to Brownian motion and to revert to their initial distribution state, with their magnetic moment becoming randomly aligned again. Neither remnant magnetization nor hysteretic effects are observed.

The alteration of the microstructure and distribution of the nanoparticles within the carrier liquid induced by the application of an external magnetic field, explains the unique field-dependent optical properties exhibited by these fluids. In particular, the refractive index [149, 150], birefringence and dichroism [151, 152] or transmittance [153, 154] of a ferrofluid depends on the magnitude and orientation of the applied magnetic field. Taking advantage of these properties, several fiber-based magnetic field sensors have already been reported [144, 145]. For instance, both extrinsic and intrinsic Fabry-Pérot interferometers have been proposed by filling a cavity, formed within the core of an optical

fiber or between two axially aligned optical fibers, with a ferrofluid and by monitoring the wavelength shift of the optical resonances induced by the field-dependent refractive index [155, 156, 157]. Multimode fibers have also been used as modal interferometers, where lower-order modes interfere with higher-order modes whose propagation constant is affected by the magnetic fluid surrounding the fiber [158]. In this configuration, bending [159] and tapering of single-mode fibers [160] has also been adopted to increase the evanescent interaction and, in turn, the sensitivity to the magnitude of the magnetic field. Sagnac interferometers have also been used to detect either the magnetic field strength or its orientation based on the variation of the birefringence and dichroism induced by the external field [161, 162].

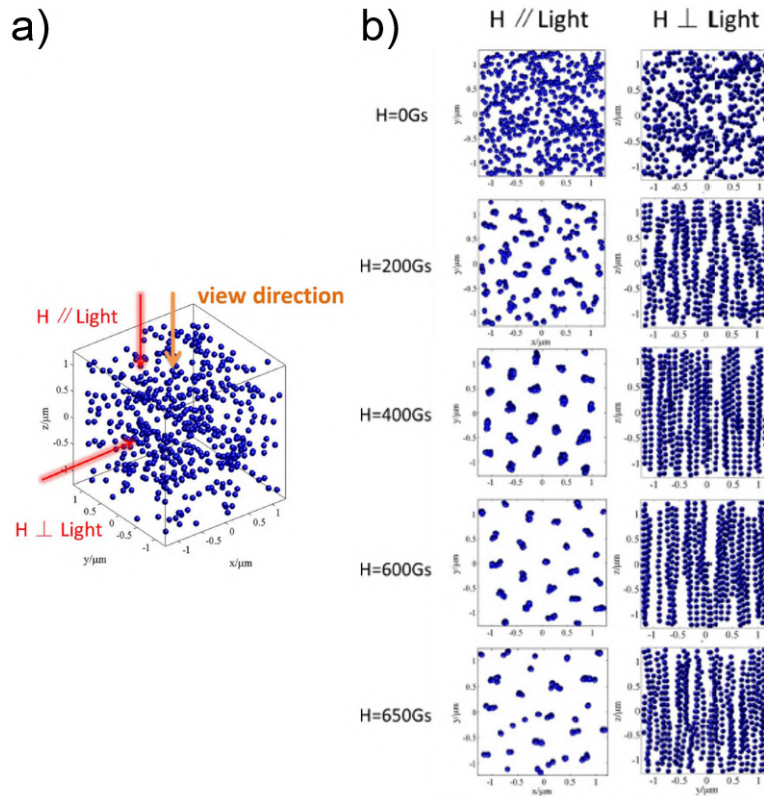


Figure 5.11: (a) Random state of magnetic nanoparticles under null field and (b) chain formation under different magnetic field directions H and magnitudes. Image was taken from [149].

Similarly, the planar-based Fabry-Pérot interferometers described throughout this chapter can also be used for magnetic field sensing. With the ferrofluid inside the microfluidic channel, the refractive index of the cavity will depend on the magnitude of the applied magnetic field which, according to equation 5.3, leads to a field-dependent resonant wavelength. Therefore, the magnitude of the external field can be measured by tracking the wavelength of one of these resonances in the reflected optical spectra. For this operation, a 5 mm long microfluidic channel with rectangular cross-section of $37\ \mu\text{m}$ by $90\ \mu\text{m}$ (width by height) was fabricated at the surface of the substrate, while a 1.2 cm long optical waveguide written $70\ \mu\text{m}$ beneath the substrate's surface orthogonally intercepted the microfluidic channel and ended $10 \pm 1\ \mu\text{m}$ from the closest sidewall; the

parameters for fs-laser direct writing and chemical etching were the same as the ones used to construct the refractometer described in section 5.2.3. Still, two important features regarding the fabrication of the device have to be addressed.

While constructing a long-period grating actuator in a single-mode fiber covered by a ferrofluid, Konstantaki *et al* [163] observed that the magnetic fluid left a residue layer over the cladding which affected the spectral properties of the grating and jeopardised the repeatability of the device. Further, Zu *et al* [164] reported that adhesion to the inner walls of a photonic crystal fiber was more likely in ferrofluids with a higher concentration of magnetic nanoparticles. Here, because the fabrication of the microfluidic channel requires chemical etching with HF acid, its inner walls present H^+ groups that aggravate this problem by causing a weak acid-base reaction between the alkaline magnetic nanoparticles (pH=8-9) and the acidic surface of the microfluidic channel. In turn, the adsorption of the nanoparticles to the sidewalls of the microfluidic channel intersecting the optical waveguide provokes optical scattering and attenuation of the incident light beam, which leads to a degradation of the measured optical signal. To solve this process, several methods have been proposed which decrease the contact angle between the ferrofluid and the fused silica surface, and minimize the wettability and adsorption of the nanoparticles to the surface. Konstantaki *et al* [163] silanized the cladding of a boron-doped germanosilicate fiber and mixed the magnetic fluid with an immiscible solution that lowered the fluid's surface tension, while Candiani *et al* [165] functionalized the inner walls of a microstructured optical fiber with polyvinylpyrrolidone that enhanced the hydrophilic properties of the silica surface. Here, to prevent the acid-base reaction and adsorption of the nanoparticles, the surface of the microfluidic channel was chemically treated with potassium hydroxide to increase the pH of its inner walls. After chemical etching with HF acid, the substrate was immersed in a potassium hydroxide solution with mass concentration of 40.02% and at a temperature of 48°C, and treated for six hours in an ultrasonic cleaner. Chemical treatment with hydrogen peroxide mixed with an alkaline or acid agent, or thermal treatment could have been used instead.

To minimize evaporation of the carrier liquid and prevent the magnetic nanoparticles from leaving the microfluidic channel under an external magnetic field, a PDMS cover layer was irreversibly bonded to the surface of the fused silica substrate, as depicted in figure 5.1. The PDMS cover was prepared and sealed to the fused silica substrate through the following protocol: (i) the elastomer and curing agent solution were mixed in a 10:1 volume ratio, respectively; (ii) the ensuing mixture was degassed in a vacuum chamber to prevent bubble formation; (iii) the resulting liquid solution was baked on a hot plate at 100°C for 40 minutes; (iv) two connection holes with diameter of 1/16" and spaced by 4.8 mm were drilled into the solid PDMS layer with a biopsy puncher to form the inlet and outlet interconnections; (v) the surfaces of the fused silica substrate and PDMS cover layer were exposed to oxygen plasma for around ten minutes in order to turn both surfaces hydrophilic; and (vi) both substrates were brought into contact and permanently bonded after aligning the interconnection holes with the microfluidic channel.

Only after both of these processes were performed was the magnetic fluid injected

inside the microfluidic channel. Water-based ferrofluids were chosen in detriment of oil-based ones as they possess a lower refractive index which increases the interferometer's finesse and makes the detection of the resonant wavelength easier, and a lower viscosity which facilitates filling the microfluidic channel. A water-based ferrofluid (EMG507, Ferrotec Inc. [166]) composed by magnetite nanoparticles (Fe_3O_4) with an average diameter of 10 nm dispersed in deionized water in a volume concentration of 0.4-1.1%, was used. At null field, its refractive index, optical attenuation and thermo-optic coefficient are 1.3413, 20.3 dB per 100 μm and -8×10^{-5} RIU/ $^\circ\text{C}$ at 1550 nm, respectively [149, 167]. A syringe connected to the inlet opening at the PDMS layer through a microfluidic tubing with outer diameter of 1/16" pumped the ferrofluid into the microfluidic channel; the fluid could exit the microfluidic channel through a similar tubing connected to the outlet. After injecting the ferrofluid, the microfluidic tubings were removed and a glass slide was placed over the PDMS layer to prevent rapid evaporation through the inlet and outlet openings. Figure 5.12(a) shows an image of the device after this procedure, with no air bubbles being observed inside the microfluidic channel.

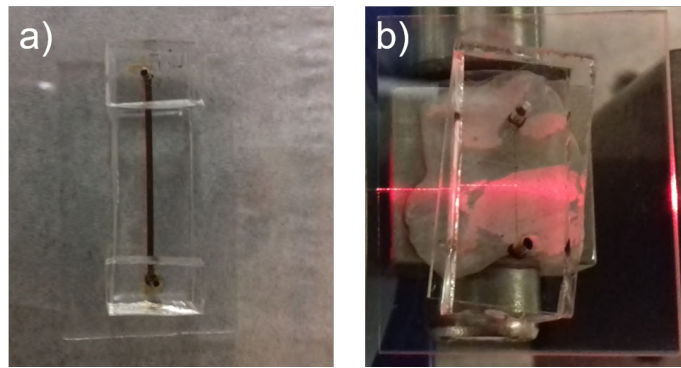


Figure 5.12: Images of the device (a) after injecting the ferrofluid inside the microfluidic channel, and (b) with a 633 nm light beam propagating throughout the fs-laser written waveguide and into the Fabry-Pérot cavity.

The device was characterized with a setup similar to the one described in figure 3.10, with the substrate being placed near a magnetic field generation coil responsible for creating a unidirectional and uniform magnetic field. The magnitude and direction of the applied magnetic field can be tuned by changing the electric current flowing through the coil and by rotating the coil in relation to the optical axis of the fs-laser written waveguide, respectively. The magnitude of the field was calibrated with a gaussmeter, with all values stated from this point forward corresponding to the magnitude of the field in the microfluidic channel. Of note, the maximum current supported by the generation coil limits the magnitude of the magnetic field to a maximum of 30.5 mT. The device was solely characterized against variations in the magnitude of the applied field, while keeping the magnetic field parallel to the direction of propagation of the light beam. A broadband source EXFO Optical System IQ-203 with an integrated ASE source module IQ-2300 and an OSA Yokogawa AQ3670D served as optical source and detector, respectively, with the reflected spectrum being measured from 1500 nm to 1600 nm with a resolution of

1 nm. In addition, the measurements were carried at a temperature of $19.0 \pm 0.5^\circ\text{C}$, which corresponds to a thermally-induced refractive index variation of $\pm 4 \times 10^{-5}$ RIU meaning, consequently, that thermal effects could be neglected. As an aside, the cross-sensitivity effect due to temperature variations could be entirely removed by writing a Bragg grating waveguide (sensitive to temperature and immune to variations of the magnetic field) within the probing waveguide [168]. It was also observed that the reflected spectrum remained stable after injecting the ferrofluid, and that the measured signal responded instantaneously when changing the magnitude of the magnetic field.

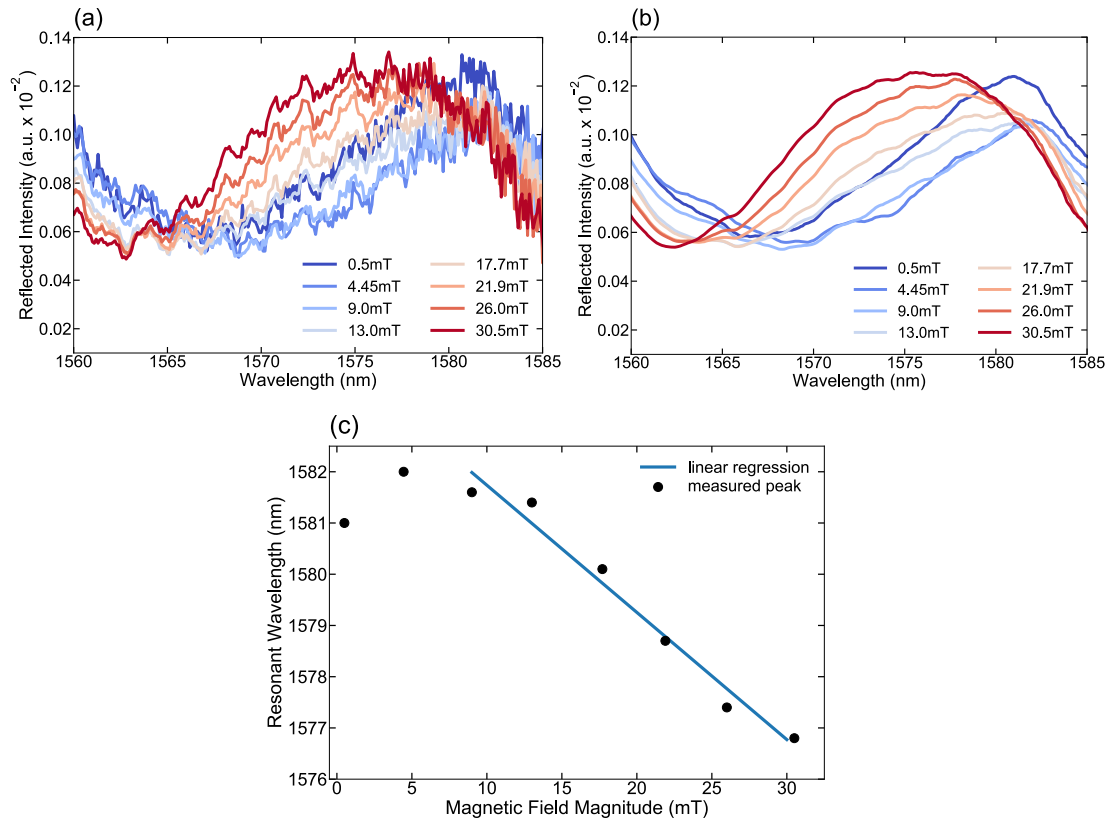


Figure 5.13: Optical characterization of the Fabry-Pérot interferometer under an external magnetic field. Measured reflected spectra (a) as measured and (b) after application of a high-pass filter to remove the noise component. (c) Evolution of the resonant wavelength with the magnitude of the magnetic field.

The gathered spectra are plotted in figure 5.13(a) for different magnitudes of the applied field. Compared to the spectra reported in section 5.2.3, the intensity of the reflected signal and the signal-to-noise ratio are much weaker which is attributed to the high attenuation losses of the magnetic fluid. Accordingly, to facilitate tracking of the resonant wavelength against the magnitude of the applied field, figure 5.13(b) also shows the measured spectra after application of a low-pass filter to remove the noise (high-frequency) components.

Increasing the magnitude of the magnetic field from 0 to 30.5 mT causes the reflected signal to shift towards lower wavelengths and its maximum reflected intensity to slightly increase. In particular, figure 5.13(c) shows the behaviour of the resonance located

at 1580 nm, where two distinct regimes are observed: the resonant wavelength barely changes for magnitudes lower than 9.0 mT, and starts to decrease linearly as the magnitude increases towards 30.5 mT. To understand this behaviour, it is important to consider the dependence of the ferrofluid's refractive index (n_{MF}) on the applied magnetic field (H), which according to Zhao *et al* [149] can be defined through the following expression:

$$n_{MF} = \begin{cases} n_0, & \text{for } H < H_c \\ (n_s - n_0) \times \left[\coth\left(\alpha \frac{H-H_c}{T}\right) - \frac{T}{\alpha(H-H_c)} \right] + n_0, & \text{for } H > H_c \end{cases} \quad (5.10)$$

where n_s is the refractive index of the ferrofluid at saturation, n_0 is the refractive index of the ferrofluid at null field, H_c is the critical field strength, α is a fitting parameter and T is the temperature [149]. The refractive index of the magnetic fluid only starts to change when the magnitude of the applied field is enough to overcome diffusive forces, defined through the critical field strength (H_c), and to induce the formation of magnetic columns. This observation explains why the resonant wavelength barely changes below 9.0 mT, which is further validated by noting that the critical field strength for the ferrofluid in cause is 11 mT at 28°C [149]. Above the critical field strength, the refractive index should follow a Langevin function, which can be simplified to a linear function for low field magnitudes (H). Noting that the saturation magnetization for the magnetic fluid EMG507 (Ferrotec Inc.) is 110 mT, the behaviour observed in figure 5.13(c) agrees with the theoretical model. After fitting the measured data from 9.0 mT to 30.5 mT with a linear regression, a sensitivity of -0.25 ± 0.02 nm/mT was obtained for this magnetic fluid, which possesses a 0.4-1.1% volume concentration. Given that in section 5.2.3 a sensitivity of 1209 ± 13 nm/RIU was obtained for a similarly-sized cavity, the refractive index of the ferrofluid decreases by around 4.45×10^{-3} from 9.0 mT to 30.5 mT. In similar fiber-based Fabry-Pérot interferometers, sensitivities of 1.21 nm/mT in the 6 to 18 mT range with a 3.9%(V/V) concentration of magnetic nanoparticles [155], and 2.3 nm/mT in the 0 to 12 mT range with a 17.7%(V/V) concentration [156] were obtained. Therefore, higher sensitivities can be obtained using ferrofluids with a higher concentration of magnetic nanoparticles at the expense of higher attenuation losses (this could nonetheless be countered by fabricating narrower cavities).

According to figure 5.13(c), the decrease of the resonant wavelength when the magnitude of the magnetic field increases means that the refractive index of the ferrofluid is lowering, which can also explain why the reflected intensity slightly increases similarly to what was observed in section 5.2.3. This, however, is contrary to what was reported in [155, 156] where the measured positive sensitivity meant that the refractive index of the ferrofluid increases with the magnitude of the applied field. The different behaviours are related to the anisotropic distribution of the nanoparticles under an external field which is summarized in figure 5.11. With the magnetic field parallel to the optical axis of the waveguide (situation described here), the magnetic nanoparticles organize in columns that grow parallel to the external field, which means that the medium as seen by the incident light beam is mainly formed by the carrier liquid and, in turn, the cavity's refractive index progressively decreases towards the refractive index of the carrier liquid

as the magnitude of the external field increases. With both fields perpendicular to each other (situation described in [155, 156]), the magnetic columns align orthogonally to the waveguide and, in turn, the incident light beam mainly sees a medium composed by magnetic nanoparticles with the cavity's refractive index increasing towards that of magnetite. The dependence of the refractive index of ferrofluids on the relative orientation between the magnetic and light fields has already been object of study in [149, 150, 169], and is also represented in equation 5.10 where a positive (negative) value of α means that both fields are perpendicular (parallel).

With the magnetic field transversal to the optical axis of the waveguide but along the substrate's plane, the nanoparticles started to agglomerate near the edges of the microfluidic channel, causing the refractive index within the region intersecting the waveguide to decrease towards the refractive index of the carrier liquid. When removing the magnetic field, because the length of the microfluidic channel is 5 mm, which is one/two orders of magnitude higher than the length of the magnetic columns, the nanoparticles could not redistribute randomly within the microfluidic channel, leading to an hysteretic effect.

Lastly, after one week, the carrier liquid fully evaporated from the cavity leaving behind a cluster of magnetic nanoparticles agglomerated at the bottom surface of the microfluidic channel. Given that the diffusion coefficient of water (the ferrofluid's carrier liquid) in PDMS and in fused silica are 10^{-9} m²/s and 10^{-17} m²/s, respectively [170, 171], it is evident that the evaporation issue resides in the PDMS. Therefore, more definite sealing methods must be used. A possible alternative is to produce an all-silica-based device by laser-welding a glass cover to the fused silica sample containing the microfluidic channel. Moreover, sedimentation of the nanoparticles also impacts the device lifetime, requiring the use of high-viscosity fluids or with a lower concentration of magnetic nanoparticles (at the expense of a lower sensitivity) to decrease the sedimentation rate [172, 173].

5.4 Conclusions

This chapter discusses the fabrication of Fabry-Pérot interferometers in a fused silica substrate through fs-laser direct writing followed by chemical etching. The proposed device consisted of a microfluidic channel operating as etalon and orthogonally intercepted by a fs-laser written waveguide, distinguishing from common planar- and fiber-based devices by making use of an optical waveguide instead of an optical fiber to launch and collect light from the interferometer. Accordingly, due to the inherent loss mechanisms of fs-laser written waveguides, a calibration of the writing parameters of the optical waveguides was needed to improve the spectral properties of the measured signal. In particular, a low signal-to-noise ratio was computed with waveguides written at high pulse energies due to the creation of defects associated with Mie scattering. These defects introduce random reflections throughout the waveguide that result in a random high-frequency modulation of the measured signal. On the other hand, the finesse quickly decreases with fs-laser written waveguides exhibiting either high coupling

or propagation losses. In particular, the waveguides must be written at low pulse energies and low translation velocities in order to enhance the signal-to-noise ratio and the finesse, respectively. Following this study, within the tested range, it was concluded that the waveguide should be written with a pulse energy of 75 nJ and translation velocity of 25 $\mu\text{m/s}$, while having the laser beam linearly polarized parallel to the scanning direction. At the same time, it was found that the optical waveguide could end 15-20 μm utmost from the microfluidic channel, without affecting the finesse of the interferometer. Meanwhile, the exposure parameters used to write the microfluidic channel can also cause imperfections at the cavity mirrors that decrease the finesse. With the microfluidic channel written by stacking multiple laser-exposure tracks, parallel interfaces with a surface roughness around tens of nanometres were obtained by writing each track with a pulse energy of 60 nJ and translation velocity of 3000 $\mu\text{m/s}$ and with a horizontal and vertical spacing between adjacent laser-exposure tracks of 3 μm and 5 μm , respectively. These conditions ensure a high etching selectivity that enables the formation of parallel mirrors, and a good vertical overlap between laser-exposure tracks that guarantees a low surface roughness. The microfluidic channel can be sealed by irreversibly bonding a PDMS cover layer to the substrate of the surface, whereas the optical waveguide can be permanently glued to an external optical fiber terminating in a V-groove block in order to form a complete lab-on-a-chip device; the refractive index of the curing glue and the pristine medium should be equal to prevent the formation of an additional Fabry-Pérot cavity.

Following this calibration of the fabrication procedure, the device was tested as a refractometer. A maximum linear sensitivity of 1209 ± 13 nm/RIU for refractive indices ranging from 1.2962 to 1.3824 (at 1550 nm) was measured for a 37 μm wide cavity. Further, due to the poor reflectivity of the cavity mirrors, it was observed a decrease in the finesse of the measured signal with the increase of the refractive index of the cavity, which limits the operation range of the optical sensor. Based on the field-dependent refractive index property of ferrofluids, the constructed Fabry-Pérot interferometers were also used to measure the magnitude of an external magnetic field by filling the microfluidic channel with a water-based ferrofluid. To avoid adhesion of the magnetic nanoparticles to the inner walls of the cavity, the surface of the microfluidic channel was chemically treated with KOH at 48°C. A linear sensitivity of -0.25 ± 0.02 nm/mT, from 9.0 to 30.5 mT, with the field parallel to the waveguide axis was measured. For comparison, sensitivities one order of magnitude higher around 1-2 nm/mT have been obtained in similar fiber-based configurations, by using ferrofluids with a higher concentration of magnetic nanoparticles instead [155, 156]. Further, the high optical absorption of the magnetic fluids significantly decreases the signal-to-noise ratio and finesse.

Despite these demonstrations, the results obtained still fall short than those reported for fiber-based Fabry-Pérot interferometers due to the higher insertion losses of the fs-laser written optical waveguides. Furthermore, by relying on a configuration where the reflectivity of each interface is determined by the Fresnel reflection coefficient, the finesse of the interferometer is inherently low. A possible method for improving the

reflectivity of each interface and, in turn, of the finesse, consists in depositing a metallic layer at the inner walls of the microfluidic channel. Nevertheless, the proposed device still has its merits as it allows the implementation of other functionalities not easily seen in fiber-based devices. Regarding the operation as magnetic field sensor, future developments include the simultaneous detection of field magnitude and orientation by making use of the dependence of the ferrofluid's refractive index with the relation between the magnetic and light fields through writing of optical waveguides spanning all spatial directions; this configuration is easier to realize in a planar geometry than in single-mode fiber Fabry-Pérot interferometers. At the same time, the applications of Fabry-Pérot interferometers go beyond optical sensing, as these structures can also be employed as optofluidic microlasers [142].

Chapter 6

Monolithic WGM Resonator

This chapter overviews the fabrication and optical characterization of a monolithic lab-on-a-chip device for label-free biosensing, based on the excitation of whispering-gallery mode resonances. The device is entirely made of fused silica and consists of a microdisk resonator coupled to a suspended waveguide, with both microstructures integrated inside a microfluidic channel for fluid handling capabilities. Whispering-gallery modes are excited by the evanescent field of a micrometric-sized circular suspended waveguide, which is anchored to the walls of the microfluidic channel. The fabrication of the device encompasses fs-laser direct writing followed by chemical etching and thermal annealing. This last step is included to decrease the surface roughness of both microstructures to a nanometric scale, thereby reducing intrinsic optical losses and increasing the quality-factor. Further, thermal-induced morphing is used to position, with submicrometric position, the suspended waveguide tangent to the microresonator to enhance the spatial overlap between the evanescent field of both optical modes. Through this approach, issues related to the structural integrity of the device and to the permanent alignment between the optical waveguide and the microresonator, which are typically encountered when coupling with tapered optical fibers and limit the application of these systems, can be overcome. The response of the device, namely sensitivity and quality-factor, to refractive index variations of the surrounding medium is studied.

6.1 Introduction

Whispering-gallery modes correspond to a discrete set of modes that can propagate along the surface of an optical microresonator [174]. These modes are confined within the microresonator due to total internal reflection at its surface, whereas the resonant wavelengths are defined by the geometry of the microresonator and by the refractive index contrast between the host material and its surroundings. WGMs have been reported in numerous geometries, such as microspheres [175], microdisks [176], microtoroids [177], microrings [178] or microbottles [179], with diameters ranging from a few micrometers to a few millimetres. These structures are usually made in fused silica or silica-derived glasses

through lithography and etching based techniques, but have also been demonstrated in crystals, polymers and even liquids [180].

The resonance and total internal reflection conditions dictate that the characteristics of the guided modes are affected by the properties of the medium surrounding the microresonator. Together with the intrinsic low losses exhibited by these structures, which translate into ultrahigh quality-factors (Q-factor) in-between 10^8 and 10^{10} , WGM microresonators constitute ideal platforms for optical sensing [181, 182]. Furthermore, the enhanced photon lifetimes, low mode volumes and strong light-matter interactions make these microstructures attractive for applications in the fields of photonics and non-linear optics [183]. In fact, a review of the literature reveals that WGM microresonators have been used to detect several physical parameters, such as temperature [184], pressure [185], electric field [186] and magnetic field [187]. Also, through chemical functionalization of the surface of the microresonator and owing to their ultrahigh Q-factors, targeted detection of single nanoparticles, molecules or viruses is possible [188]. Moreover, the progress made in signal enhancement techniques has contributed to rapid advances in the construction of optical sensors [189]. Besides the typical schemes involving measurement of the variation in the resonant wavelength or intensity, detection through mode splitting or mode broadening has also been adopted for self-referenced measurements where unwanted fluctuations caused by thermal cross-talk are removed. An enhancement in the sensitivity has also been verified by integrating WGMs with surface plasmon resonances. Meanwhile, doping the host medium or functionalization of the microresonator's surface with optical gain materials (for instance, rare-earth materials) has led to the construction of narrow-linewidth microlasers with low-threshold pump powers of a few microwatts. Due to their strong light-matter interactions, non-linear effects have also been explored in optical microresonators formed on either centrosymmetric (lithium niobate or beat barium borate) or non-centrosymmetric materials (fused silica or fluoride crystals) [190].

The excitation of WGMs requires near-perfect phase matching conditions between the propagation constants of the excitation/coupling mode and the WGM, and for both to spatially overlap [191]. These requirements are hardly met through free-space coupling, which proves to be an inefficient process. Instead, methods based on evanescent coupling through either prism couplers, adjacent waveguides or tapered fibers [191, 192, 193], are typically employed as illustrated in figure 6.1. Prism couplers rely on frustrated total reflection at the base of a high-index prism, which generates an evanescent field that can excite the WGMs of the microresonator. Phase-matching can be reached by properly designing the prism and by correctly tuning the angle of incidence. Still, although efficient and selective, this coupling configuration is bulky. Tapered fibers, on the other hand, are more flexible and easier to align with the optical microresonators. These structures are usually fabricated by heating and stretching a single-mode fiber, resulting in a millimetre or centimetre-long tapered section with waist diameter around 2-5 μm . Within the taper, light is guided by the cladding-air interface which, together with the low diameter, enlarges the evanescent field of the propagating optical mode thereby enhancing its spatial overlap

with the WGM field. The tapered fiber supports multimode propagation, but, in the case of an adiabatic taper, only its fundamental mode is guided. The propagation constant of the guided mode (or modes) mainly depends on the diameter of the taper, which allows, by correctly designing the taper, an efficient coupling with any particular mode of interest. Side-polished and angled-tip optical fibers have also been used to excite WGMs. However, with these structures, phase-matching is perfect only in the limit of large sphere sizes, with the coupling efficiency being 20% for spheres with a diameter of 1 mm, and much lower for smaller spheres [193].

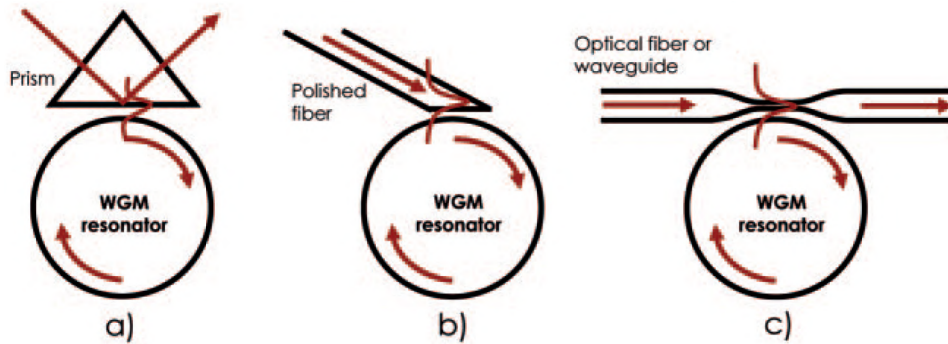


Figure 6.1: Techniques used for excitation of whispering gallery mode resonances: (a) prism coupling using frustrated total internal reflection, (b) slant-cut optical fiber coupling, and (c) tapered fiber or optical waveguide coupling. Image was taken from [194].

Despite all the extensive research conducted on the topic, practical issues regarding sample handling, connectivity, robustness, portability or easiness of use still limit the widespread use of these devices in biosensing applications. In fact, these issues are seldom considered when designing the device, and are primarily caused by the excitation setup itself. The lack of integration between the prism coupler or tapered fiber and the optical microresonator limits the portability and handling of the device, while associated mechanical instabilities also affect the excitation of WGMs. Further, the incompatibility between traditional processing techniques prevents the integration of these optical devices with microfluidic systems capable of handling low volumes of analyte, which is appealing for biosensing and in medical environments.

Even though fs-laser micromachining can solve most of these issues by integrating all components in either a lab-on-a-chip or lab-on-a-fiber architecture, only a few number of reports have discussed this form of construction. Two-photon polymerization has been used to fabricate WGM resonators at the tip of multicore optical fibers for vapour [195] and temperature sensing [196], as illustrated in figure 6.2(a). The device consists of two microprisms, each fabricated over one core of the fiber, which are linked by a 20 μm long tapered waveguide with a rounded-rectangular waist cross-section of $1 \times 1 \mu\text{m}^2$. A microring [195] or microdisk [196] resonator, with external diameter of 30 μm and 40 μm respectively, are also fabricated through two-photon polymerization and put in contact with the tapered waveguide at the waist region. Light propagating through one of the fiber cores is coupled via a microprism into the tapered waveguide, which evanescently excites the WGM resonances of the microresonator, before being coupled through the

second prism to the other fiber core, with the transmitted spectrum being measured at its output. Although it is compact and provides stable operation, this approach, nevertheless, lacks the integration with microfluidics.

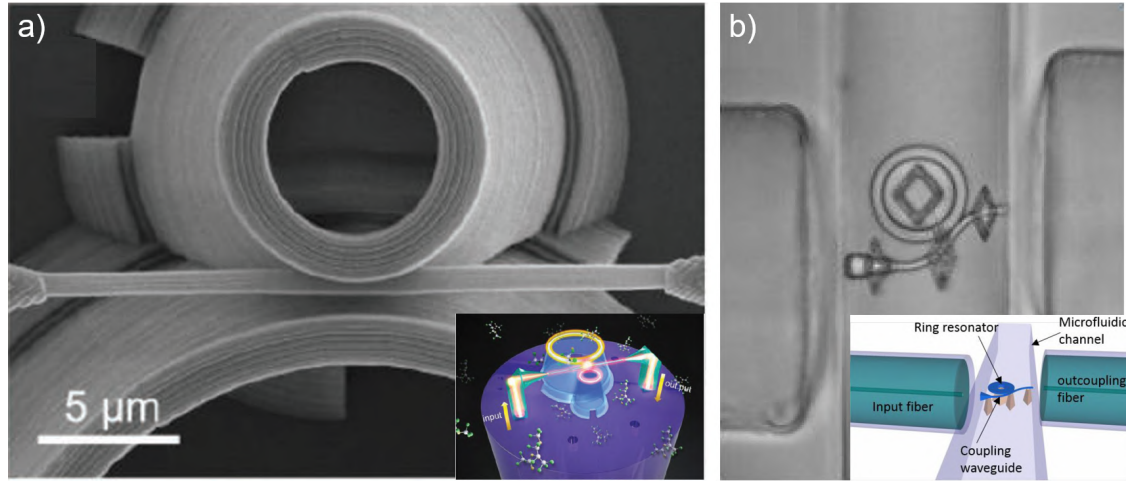


Figure 6.2: Examples of WGM resonators fabricated through multiphoton polymerization assisted by fs-laser irradiation and coupled to a polymeric suspended waveguide. (a) Top view SEM image of a microring resonator fabricated at the tip of a microstructured optical fiber and excited by a coupling polymeric waveguide. (b) Top view image of a microring resonator fabricated inside a microfluidic channel made through fs-laser direct writing followed by chemical etching on a fused silica substrate, and excited by a suspended waveguide coupled to a lead-in and lead-out optical fiber. The inset shows the schematics of the respective devices. Image (a) was taken from [195], and image (b) from [67].

Regarding lab-on-a-chip devices, Kelemen *et al* [67] combined fs-laser direct writing followed by chemical etching with two-photon polymerization to fabricate a free-standing microring resonator coupled to a suspended waveguide, within a microfluidic channel, as depicted in figure 6.2(b). The microfluidic channel is embedded in a fused silica substrate and contains a polymeric microring resonator, with external diameter of 50 μm , in contact with a 90 μm long bended polymeric core, which is anchored to both walls of the microfluidic channel and is responsible for evanescently exciting WGMs of the microring. To improve the mechanical stability, both microstructures are supported by thin pedestals. Light is coupled into and out of the suspended waveguide by two optical fibers, which are fitted in a respective groove, also machined within the substrate through fs-laser direct writing followed by chemical etching, aligned with the suspended waveguide and glued to the walls of the groove. Further, different fluids can be injected inside (or removed from) the microfluidic channel through two PEEK tubes that are glued to respective reservoirs, which connect the microfluidic channel to the surface of the chip. Besides operation as a refractometer, biosensing was also demonstrated in this device by functionalizing the surface of the resonator with biotin and detecting the binding of streptavidin protein to it.

However, the former devices rely on polymeric-based microresonators and coupling waveguides which may compromise the performance and application of the device, especially when compared to its silica-based counterparts. Fused silica, besides being the material of choice in optical communications, is also attractive for biosensing and

biomedical applications due to its biocompatibility and inertness to solvents. Further, its mechanical durability and thermal stability is a pre-requisite in most real-life applications. Nevertheless, the fabrication of the previous geometries in fused silica has proven to be a challenge owing to the subtractive nature of fs-laser irradiation followed by chemical etching. Indeed, the closest demonstration was reported by Song *et al* [61], where a tapered fiber was welded via CO₂ laser irradiation to the surface of a microtoroid resonator, previously fabricated inside a microfluidic channel and with diameter and height of 80 μm and 10 μm , respectively. Following fabrication, the device was tested as a refractive index sensor. Still, this approach resulted in the deformation of the waveguide's cross-section (the original circular cross-section became compressed flat-oblate) which decreased the Q-factor when compared to the results obtained through coupling with a free-standing tapered fiber.

Accordingly, the main objective of this work was to fabricate through fs-laser micromachining an integrated optofluidic device, entirely made of fused silica, for label-free sensing based on WGM resonances. A schematic of the device is designed in figure 6.3. It is composed by a microfluidic channel that contains a microdisk, supported by a cylindrical pedestal of lower radius, and a suspended waveguide anchored to the lateral walls of the microfluidic channel and permanently coupled to the microresonator. The microfluidic channel is formed at the surface of a fused silica chip and is responsible for the fluid handling capabilities, whereas the suspended waveguide is tangent to the microresonator and excites the WGMs of the microdisk through evanescent coupling. A lead-in and lead-out waveguide, fabricated through fs-laser direct writing, drive light into and out of the suspended waveguide, respectively. The fabrication process consists of three main steps: (1) fs-laser direct writing followed by chemical etching of the irradiated areas to create the microfluidic channel (already including the microdisk and the suspended waveguide), (2) thermal annealing of the substrate, and (3) fs-laser direct writing of the lead-in and lead-out waveguides. This methodology allows overcoming most issues typically encountered when machining fused silica and enables the construction of a monolithic device, while providing a wide control over the dimensions and geometry of the microstructure.

The chapter is organized as follows. After this introductory section, it is provided a theoretical background about the excitation and propagation of WGMs in optical microresonators. General considerations concerning the fabrication of the device are then made following from this analysis. The fabrication of the suspended waveguides and coupling with the lead-in and lead-out waveguides is then discussed. This is complemented by examining the coupling and propagation losses of the suspended waveguides against different external fluids. Afterwards, it is described the fabrication of the microdisk and its integration with suspended waveguides for efficient excitation of WGMs. The response of the device against variations of the refractive index of the fluid surrounding the microresonator is also studied. Lastly, some final remarks summarizing the results obtained and regarding future improvements are made.

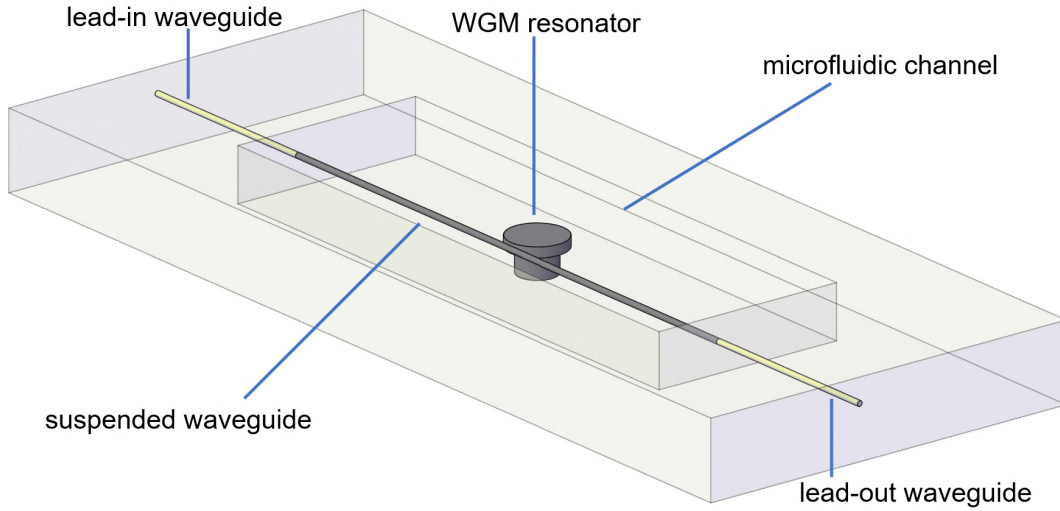


Figure 6.3: Schematic of the device.

6.2 Theoretical Background

As mentioned earlier, WGMs correspond to specific resonances of a wave field that circulates near the surface of a resonator based on continuous total internal reflection. Due to the circular symmetry of the microresonators, a spherical coordinate system is generally used to analyse the WGMs. In particular, their spatial structure is characterized by a unique set of number (q, l, m) which correspond to the radial, polar and azimuthal numbers, respectively, and by the polarization of the WGM, which can be transverse electric (TE) or transverse magnetic (TM) [180, 197]. TE modes have the electric field parallel to the optical axis of the resonator, with the optical axis defined as the axis in which the structure shows rotational symmetry, *i.e.* the electric field is tangent to the sidewall of the resonator, while TM modes have the electric field orthogonal to this surface. The spectral location of each mode is defined by the resonance condition, which imposes each propagating wave to interfere constructively with itself after one round-trip across the surface of the microresonator. Generally, for modes propagating around the equator of a microresonator with circular boundary, this condition is expressed as:

$$\lambda_{res} = \frac{2\pi R n_{eff}}{m} \quad (6.1)$$

where λ_{res} is the resonant wavelength, R is the surface radius, n_{eff} is the effective refractive index of the WGM under analysis and m is its azimuthal number. Accordingly, the resonant wavelengths depend on the refractive index contrast between the microresonator and its surrounding environment and on the geometry and size of the microresonator. These modes can be experimentally identified by combining analysis of the frequency spectrum with far-field imaging [198]. A depiction of the first few modes of a microdisk resonator is shown in figure 6.4. The radial number (q) corresponds to the number of field maxima along the radial direction, whereas the azimuthal number (m) coincides with the number of field maximum along the resonator's perimeter. Another parameter (p), defined as $p = l - |m|$ and corresponding to the angular mode number,

is related to the number of oscillations along the polar direction (vertical direction perpendicular to the equatorial plane) [198]. The fundamental mode is characterized by $q = 1$ and $p = 0$, whereas higher-order modes are associated to $q > 1$ and/or $p > 0$. Consecutive modes of the same family (pq) are spectrally separated by the free spectral range (f_{sr}), which is commonly defined as:

$$f_{sr} = \frac{\lambda_{res}^2}{2\pi R n_{eff}} \quad (6.2)$$

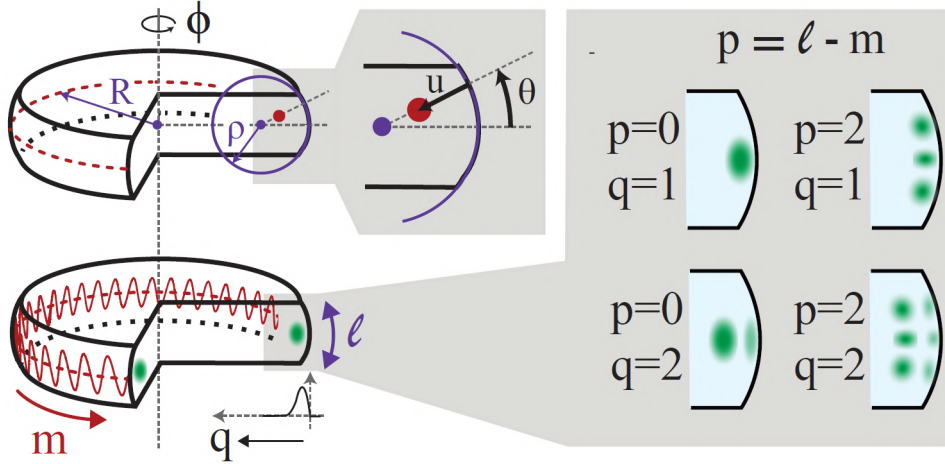


Figure 6.4: Spatial profile of WGM resonances of a microdisk resonator. Image was taken from [198].

Similar to an optical waveguide, as the microresonator increases in size, more modes are supported and the effective refractive index of the fundamental mode tends to the refractive index of the host material [193, 199]. WGMs progressively shift towards the resonator's centre as the radial number increases, while they become closer to the resonator's surface with increasing polar numbers [198, 200]. For a spherical resonator with no eccentricity, WGMs possess a $2l + 1$ degeneracy with respect to the azimuthal mode number [180, 191]. Also, only even polar order modes (symmetric modes) can be excited if the coupling waveguide is located in the equatorial plane of a spherical resonator, whereas odd polar order modes (asymmetric modes) can be excited if this condition is not verified [180, 191]. Further, in a microdisk resonator, the pedestal must have a lower diameter than that of the microdisk or a lower refractive index than that of the host material, to avoid perturbation of the WGMs and prevent coupling of light into the pedestal [199].

The coupling efficiency is defined as the percentage of power coupled into the microresonator from the coupling waveguide. Several authors have numerically studied the coupling efficiency in microdisks, microrings or microspheres [191, 200]. Generally, the coupling coefficient (κ) from the coupling waveguide to a microresonator is expressed as:

$$\kappa = \frac{\omega \epsilon_0}{4} (n_s^2 - n_0^2) N_{wvg} N_{res} \iiint_V (E_f^t \cdot E_s^{t*} + E_f^z \cdot E_s^{z*}) \exp^{i\Delta\beta z} dx dy dz \quad (6.3)$$

where ω is the frequency, ε_0 is the vacuum electrical permittivity, n_s and n_0 are the refractive indices of the microresonator and its surroundings, $E_{f(s)}^t$ and $E_{f(s)}^z$ are the transverse and longitudinal components of the electric field of the coupling waveguide (WGMs of the microresonator), $\Delta\beta$ is the difference in propagation constants of the two modes under consideration, z is the propagation direction and the integral is performed over the volume of the microresonator [191]. This equation shows that to efficiently excite WGMs, the propagation constant of the waveguide mode should equal the propagation constant of the WGM under consideration and their respective fields should spatially overlap. Phase-matching conditions are easier to be attained if the microresonator and coupling waveguide are made from the same material (an advantage of the proposed configuration), whereas a larger field overlap can be obtained by reducing the refractive index contrast between the microresonator and its surroundings or by decreasing the diameter of the coupling waveguide.

Humphrey *et al* [191] demonstrated that, for optimum coupling, the radius of the waveguide (or tapered fiber) should be 70% of the phase-matching radius. In particular, the coupling strength is roughly doubled by using the optimal radius instead of the phase-matched one. This is due to the interplay between phase-matching and field overlap. As the waveguide radius decreases below the phase-matched radius, the increase in spatial overlap dominates over the reduced phase-matching, resulting in an enhancement of the coupling coefficient until the optimal coupling radius is obtained. For radii lower than the optimal radius, phase mismatch becomes the dominant effect, causing the coupling coefficient to decrease. For radii greater than the phase-matched radius, increasing phase-mismatch and reduced field overlap cause the coupling coefficient to decrease as well.

Generally, the coupling coefficient decreases as the gap between the coupling waveguide and the microresonator widens due to poorer spatial overlap, and increases with the probe wavelength due to enlargement of the evanescent fields [200]. The geometry of the microresonator also impacts the coupling coefficient. Due to the curvature of the microresonator, the effective length over which coupling takes place is much smaller than the radius of the microresonator [197]. Further, bended waveguides are associated to a lower coupling coefficient due to mismatch between the propagation direction [200]. The coupling coefficient also depends on the polarization of the WGM, if TE or TM.

Coupling to higher-order radial modes requires smaller taper diameters than for coupling to the fundamental mode owing to a decreasing effective refractive index, but may exhibit higher coupling coefficients due to the larger evanescent field [191, 193]. The optimal coupling radius of higher polar order modes barely changes due to the similar propagation constants, but the coupling efficiency is weaker due to the narrower spatial overlap [191]. Also, smaller microresonators lead to a reduction in the optimal waveguide radius, in order to compensate for the decrease in the effective refractive index of the WGM (under consideration), and to an increase in the coupling coefficient due to larger spatial overlap [191].

One of the key parameters for optical resonators is their Q-factor (specific for

each WGM), which depends on intrinsic losses of the microresonator and on extrinsic losses. The full Q-factor is therefore a combination of multiple factors, and is expressed as follows:

$$\frac{1}{Q} = \frac{1}{Q_{mat}} + \frac{1}{Q_{rad}} + \frac{1}{Q_{scattering}} + \frac{1}{Q_{ext}} \quad (6.4)$$

where Q_{mat} is the loss due to bulk material absorption, Q_{rad} is the radiation loss, $Q_{scattering}$ is the loss due to surface scattering, and Q_{ext} corresponds to the extrinsic losses which are related to the coupling coefficient [180]. Although not disclosed in the expression above, the Q-factor may also be affected by surface contamination, by refractive index inhomogeneities, or by coupling effects to the underlying substrate or pedestal.

The absorption loss can be expressed as $Q_{mat} = 2\pi n_{eff} / (F_r \alpha_r + F_m \alpha_m) \lambda$ where F and α are the fractions of optical power circulating inside the resonator and the cladding medium and respective linear absorptions, and n_{eff} is the effective refractive index of the excited WGM [180]. Here, this term can be overlooked given that fused silica and the tested fluids show negligible absorption at the infrared wavelengths used.

Radiation losses are associated to bending losses caused by the curvature of the microresonator. These losses can be neglected for millimetre-wide resonators, but are the primary loss source for micrometer-sized resonators. [201]. Although these losses can be decreased by enhancing the refractive index contrast between the microresonator and its surroundings, this correction dictates that the microresonator-to-waveguide gap has to be smaller in order to compensate for the stronger mode confinement and to have efficient coupling.

Losses due to scattering are related to the roughness of the microresonator's surface. Numerical simulations predict that the Q-factor decreases quadratically as the surface roughness grows (see equations 1 and 2 of [201]). This was also verified experimentally [201], where it was added that an abrupt increase of the Q-factor occurs when the roughness decreases below $\lambda/20$, where λ is the probe wavelength [202]. Therefore, the surface of the microresonator should be as smooth as possible in order to maximize its Q-factor. For instance, considering losses only due to surface scattering, Q-factors of 10^{12} at 1550 nm require the root-mean square surface roughness to be lower than 2 nm [201]. Similarly, the presence of a corrugated profile at the surface of the suspended waveguide will also increase its propagation losses, and degrade the signal-to-noise ratio. One of the limitations of machining fused silica is related to the existence of residual surface roughness around 100-200 nm after chemical etching. Therefore, to obtain microstructures with high surface quality, it is necessary to realize a post-fabrication thermal treatment, either through thermal annealing, CO₂ laser irradiation, or exposure to an oxyhydrogen flame. In comparison, tapered fibers or structures fabricated through two-photon polymerization show a far smoother surface profile. Additionally, microrings typically exhibit lower Q-factors than microdisks and microtoroids, due to the presence of the inner rim which makes the WGMs more sensitive to surface imperfections [199, 200].

The external Q-factor can be defined as $Q_{ext} = m\pi/\kappa^2$ where κ is the coupling

coefficient and m is the azimuthal mode order [180]. Depending on the coupling coefficient κ , which is itself related to the distance between the coupling waveguide and the microresonator, three different regimes can be obtained [203, 204]. If the coupling waveguide is distanced by tens of micrometers from the microresonator, the coupling coefficient is too low. However, this regime results in a high external Q-factor, as can be observed from the equation above. Still, almost no power is coupled to the microresonator which leads to a low extinction ratio (*i.e.* the ratio between the power transmitted at the resonant wavelength and the power transmitted off-resonance is minimum). As the coupling waveguide gets closer to the microresonator, the coupling coefficient κ increases which leads to a decrease of the external Q-factor and to an increase in the extinction ratio. When the extinction ratio is maximum, *i.e.* when the power transmitted on resonance is null, the device is said to be operating in the critical coupling regime. The overcoupling regime is reached if the distance between the coupling waveguide and the microresonator keeps decreasing past this point, or if both structures are put in contact with one another. In this regime, the coupling coefficient increases due to the higher spatial overlap, but the external Q-factor continues to decrease. Further, despite the higher coupling coefficient, light coupled into the microresonator can recouple back into the waveguide which leads to a decrease in the extinction ratio as well. Also, in this regime, higher-order modes are observed more easily in the transmission spectrum.

Based on these considerations, the diameter of the suspended waveguide should be between 1 μm and 3 μm to maximize the spatial overlap between the mode supported by the waveguide and by the excited WGM of the microresonator. These range of diameters are also commonly used in applications where the WGMs of an optical microresonator are excited by the evanescent field of a tapered fiber. Further, precise control of the gap between the coupling waveguide and the microresonator is needed in order to maximize the external Q-factor and the extinction ratio simultaneously. For the range of diameters of the suspended waveguide considered in this work, the gap between the waveguide and the microdisk should be around 200-400 nm to operate in the critical coupling regime [204]. Still, it is important to note that a higher coupling coefficient is obtained if this distance is shortened at the expense of a lower Q-factor (operation in the overcoupling regime), and a higher Q-factor is obtained if both structures are further distanced from one another at the expense of a much lower extinction ratio (operation in the undercoupling regime).

6.3 Suspended Waveguides

The first objective is the fabrication of suspended waveguides inside a microfluidic channel. These consist of a fused silica rod suspended inside a microfluidic channel and attached to its lateral walls. This rod will act as the waveguide core, while the fluid covering the channel will serve as cladding. Coupling of light into or out of the suspended waveguide is guaranteed by two fs-laser written waveguides, which extend from the microfluidic channel wall, containing the suspended waveguide, to the fused silica substrate facet. Light is coupled into or out of the device by aligning an optical fiber

to the fs-laser written waveguide, while the fiber's free end is connected to a light source or optical detector, respectively. The section is divided in two separate parts: (i) fabrication of the suspended waveguide inside the microfluidic channel, and (ii) fs-laser writing of two optical waveguides aligned with the suspended waveguide and measurement of the insertion losses of the suspended waveguide.

6.3.1 Fabrication

The principle behind the fabrication of suspended waveguides is that of selective etching, where the fs-laser irradiated regions are etched in hydrofluoric acid at a much higher rate than the pristine material. As discussed previously, this same principle can be used to fabricate microfluidic channels, where a hollow cavity is formed at the surface of a fused silica slab after writing uniformly spaced exposure tracks that cover the full extent of the channel. Here, because the objective is to have a silica rod suspended across the microfluidic channel, the irradiation pattern has to be changed. It is important to note that the employed fabrication technique is a subtractive one, meaning that the suspended waveguide and the microfluidic channel must be, inevitably, fabricated simultaneously. This brings some difficulties which are not observed when fabricating through additive techniques, such as multiphoton polymerization.

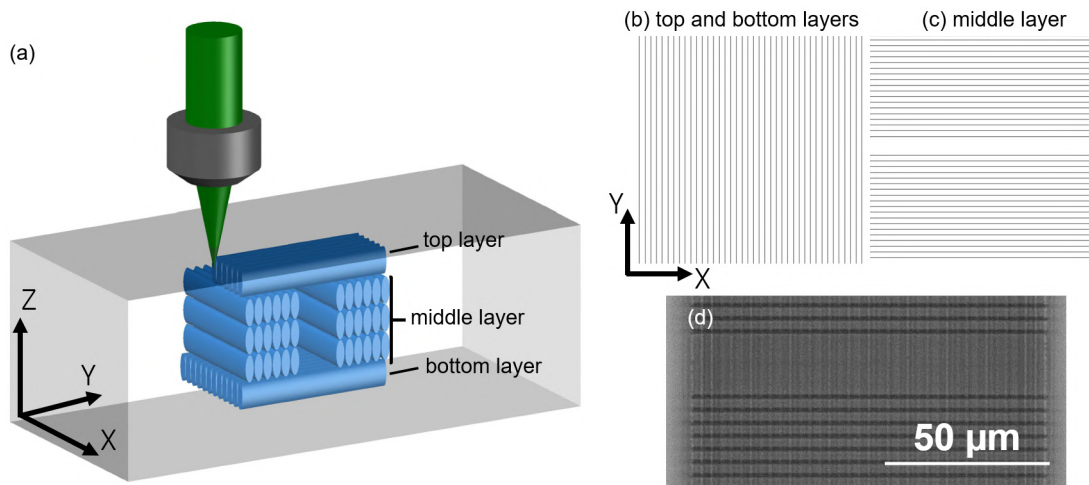


Figure 6.5: (a) Illustration of the writing configuration for the suspended waveguides, and top view path of the laser-exposure tracks for (b) the top and bottom layers and (c) the middle layers. (d) Top view microscope image of a 100 μm long suspended waveguide.

The irradiation layout used to draw the suspended waveguides is shown in figure 6.5, together with a top view image obtained after laser direct writing. The design is sliced in several horizontal planes, which are then hatched by multiple uniformly spaced lines that correspond to the path of the fs-laser beam. The layers are written following a bottom-to-top approach and, within each layer, all scans follow the same direction. The laser pulse energy, scanning speed, vertical and horizontal spacing and the orientation of the scans can be tuned for each layer. Nevertheless, here, each exposure line was written with a pulse energy of 60 nJ, scanning speed of 3000 $\mu\text{m}/\text{s}$ and with the laser

beam polarization orthogonal to the scanning direction. The remaining parameters are adjusted according to the layer and the waveguide dimensions. Considering again the waveguide design, three different types of layers can be distinguished, which are marked as bottom, middle and top layers in figure 6.5(a-c).

For bottom layers, which correspond to the layers beneath the suspended waveguide, one concern is the orientation of the exposure lines and of the beam's polarization. If the exposure lines are oriented parallel to the waveguide axis (along X in figure 6.5), the etchant cannot break through the layers immediately beneath the waveguide, and ergo remove them in suitable time. Due to the longer etching time, the waveguide cross-section may become asymmetric or, in a more severe case, it may completely dissolve before removing the material underneath it. Even with the exposure lines perpendicular to the waveguide axis, a similar effect occurs if the beam polarization is parallel to the scanning direction due to the orientation of the nanogratings. Therefore, to facilitate the etching reaction, the exposure lines must be written orthogonal to the waveguide axis (along Y in figure 6.5), and with the laser beam polarization perpendicular to the scanning direction. Although the former condition is essential, it still leads to the formation of periodically spaced crests in the waveguide's bottom surface, as will be discussed shortly. The pulse energy and scanning speed can also be changed to further enhance the etch rate.

The middle layers coincide with the layers that encompass the waveguide itself. Each of these layers includes a blank gap related to the width of the waveguide, while the number of layers times the vertical spacing between each is related to its height. The orientation of the exposure lines and the spacing between each also affects the waveguide's surface roughness. Figure 6.6(a-b) shows a top view microscope image of the suspended waveguide, which reveals that the waveguide's lateral walls appear smoother when the exposure lines are oriented longitudinal to the waveguide axis (along X in figure 6.5) than when they are scanned transversal to it (along Y in figure 6.5). Therefore, the exposure lines have to be written parallel to the waveguide axis. Nevertheless, observations made with scanning electron microscopy still reveal an existent relief pattern. With this design, the waveguide possesses a square- or rectangular-shaped cross-section after etching. Rounder waveguides could also be obtained if the width of the blank gap in each plane is changed from layer to layer, while following a circular or elliptical path.

For the top layers, which comprise the layers written above the suspended waveguide, the proposed design is the one that minimizes the duration of the laser direct writing process. Accordingly, the exposure lines are written perpendicular to the waveguide axis. Some alterations can still be made to the design in order to further decrease the duration of the writing process. Despite the more design freedom relative to the middle and bottom layers, it must be pointed out that the orientation of the exposure lines and its spacing will also affect the roughness of the waveguide's top surface. Similar to what was said regarding the bottom layers, a relief pattern resembling that of an optical grating is observed in the waveguide's top surface, as shown in figure 6.6. This pattern is visible regardless of the direction of the exposure tracks.

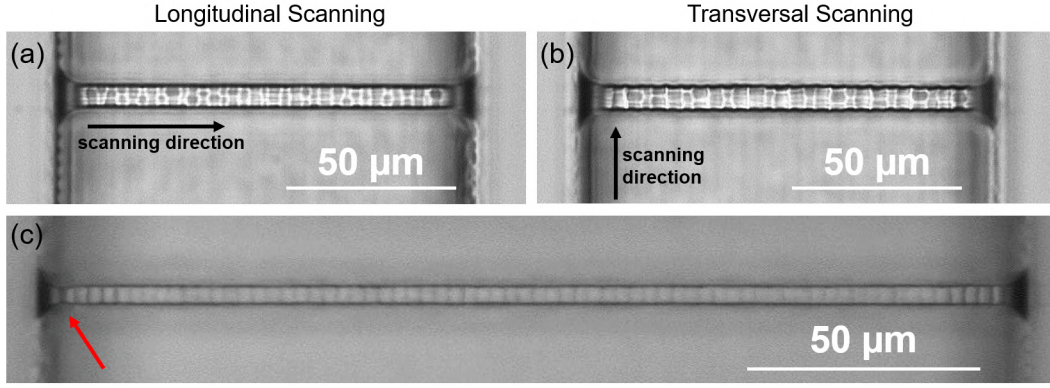


Figure 6.6: Effect of (a,c) longitudinal and (b) transversal scanning on the sidewall roughness of the suspended waveguides. Image (c) also shows that the suspended waveguide is slightly deformed at its left end (marked with an arrow) as a result of non-uniform laser exposure.

The waveguide dimensions and geometry are important when considering how light is guided across it. For instance, the size of the waveguide will define if it is monomode or multimode, whereas optical birefringence can be introduced by designing asymmetrically shaped waveguides. To discuss its size and shape, several waveguides (numbered from #1 to #13) with width and height spanning from 5 μm to 60 μm and 20 μm to 56 μm , respectively, were fabricated. The dimensions of the waveguide were measured through optical microscopy after laser direct writing and during chemical etching with HF acid, and the obtained results are shown in figure 6.7. The width and height are measured directly from the collected top and side view images, respectively; the suspended waveguide is fabricated 30 μm from a polished facet of the substrate in order to image its sidewall.

Figure 6.7 shows a slight mismatch between the waveguide dimensions defined in the design and after laser direct writing, where the final width and height are smaller by 0.9 μm and 9.3 μm , respectively. Revisiting the cross-section of a single exposure track, it resembles an ellipse with lengths of 2 μm by 11 μm along the minor and major axis, respectively. These values are similar to the measured offsets, from which it is concluded that the width (w_{design}) and height (h_{design}) of the waveguide, after laser direct writing, are given by:

$$w_{design} = gap - w_{single-track} \quad (6.5)$$

$$h_{design} = N \times dz - h_{single-track} \quad (6.6)$$

where gap is the width of the suspended waveguide defined in the middle layer (figure 6.5), N is the number of planes and dz the spacing between each plane corresponding to the middle layers, and $w_{single-track}$ and $h_{single-track}$ are the width and height of a single exposure line, respectively. The length of the suspended waveguide equals the width of the microfluidic channel.

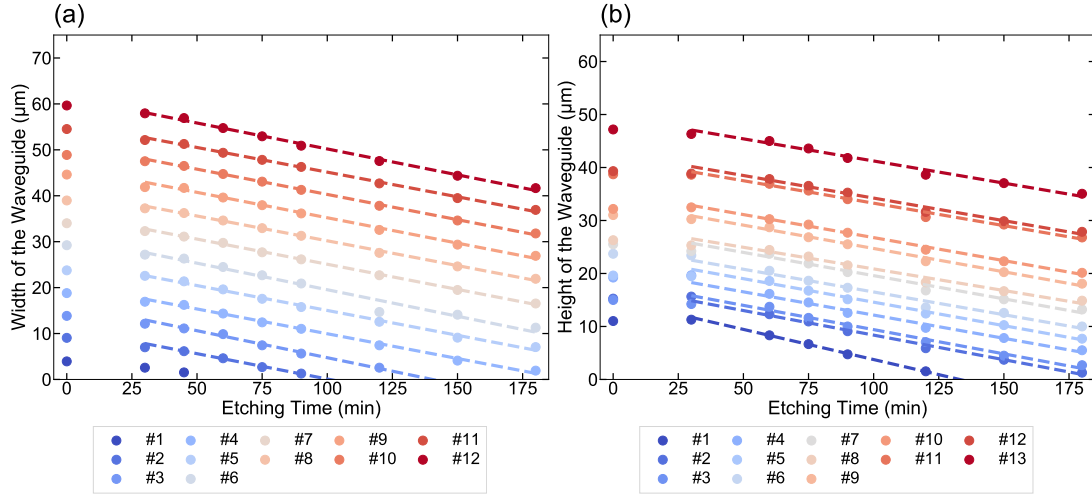


Figure 6.7: Evolution of the suspended waveguide's (a) width and (b) height during the chemical etching reaction. The marked dots correspond to the experimental data, and the dashed line to a linear fit performed to the data points.

Still, these dimensions decrease during chemical etching as demonstrated in figure 6.7, where two different behaviours are observed. In the first 30 minutes of the etching reaction the waveguide dimensions barely change, while from then on both the waveguide's width and height decrease linearly with the etching time. In the first region (first 30 minutes), the size of the waveguide is kept constant, because the hydrofluoric acid is still etching the top layers and has yet to reach the suspended waveguide itself. In the second region (30 minutes onwards), the suspended waveguide is exposed, *i.e.* it is completely surrounded by the etchant. Here, it is expected the waveguide's width and height to decrease at double the etch rate of the pristine medium. In fact, after modelling the measured data with a linear regression, it is concluded that the width and height decrease by $0.111 \pm 0.003 \mu\text{m}/\text{min}$ and $0.089 \pm 0.005 \mu\text{m}/\text{min}$, respectively, similarly to what is expected. By using a diluted etchant with a lower etch rate, the waveguide dimensions and, in turn, its waveguiding properties can be fine-tuned by extending the etching reaction.

After chemical etching, the cross-section of the suspended waveguide is square or rectangular shaped, depending if the width and height are equal or not. Further, with the exception of its terminations near the microfluidic channel walls, the dimensions of the suspended waveguide remain constant throughout its entire length, having observed this for a waveguide with maximum length of 5 mm. Also, given the small height of the suspended waveguides and the high etching selectivity, the waveguide's sidewall remains straight. For higher waveguides, though, this issue cannot be overlooked and it is expected the sidewall to become oblique. Moreover, by prolonging the etching reaction, the edges of the waveguide would start to fillet, *i.e.* to become round-shaped. From figure 6.6(c), the waveguide is narrower in the border corresponding to where the laser-exposure track starts, whereas this issue is not visible on the other end. This trait should be a result of a slight asynchronism between the trigger of the laser beam and the linear translation stage, or due to the finite acceleration of the linear translation

stage which causes the laser beam to overwrite in one of the channel borders. Another issue regarding the device handling and cleaning must also be addressed: because the waveguide dimensions are in the micrometric range, it was noticed that the suspended waveguides would easily break when drying them with a nitrogen spray gun. To prevent this, the device is instead dried in a hot plate at 110°C.

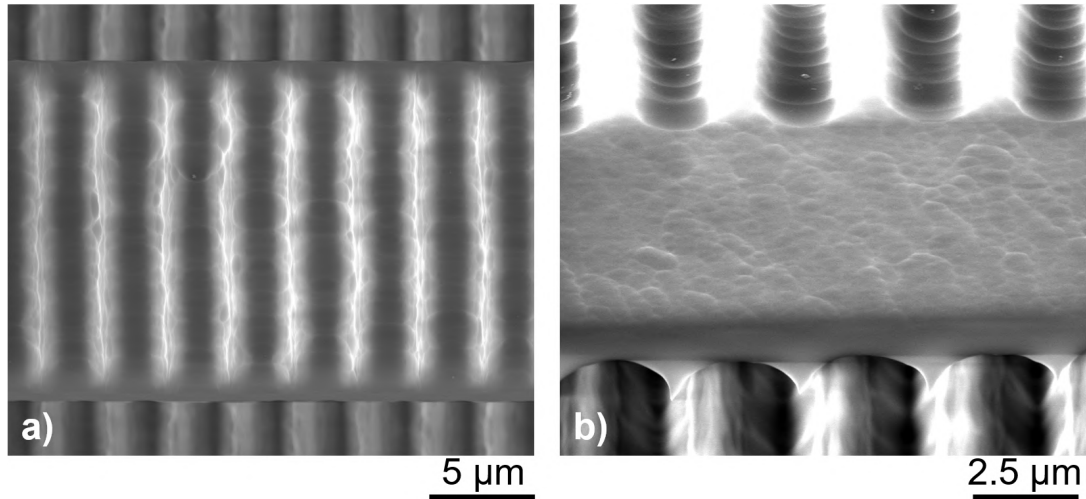


Figure 6.8: SEM images of the (a) top surface and (b) sidewall of the suspended waveguide after chemical etching. Figure (a) corresponds to a top view image, and figure (b) to an oblique view.

As suggested in figure 6.6 and confirmed in figure 6.8(a), the top surface of the suspended waveguide reveals uniformly spaced crests after chemical etching with a period that matches the horizontal spacing between exposure lines (*i.e.* 3 μm). From figure 6.8(b), the sidewall of the suspended waveguide reveals a smoother and more random pattern. Because the chosen vertical spacing of 5 μm is smaller than the height of a single exposure line (11 μm), the irradiated tracks of vertically separated layers merge during laser direct writing. The etching is then more uniform along this direction and, in consequence, the roughness is lower along the vertical walls than in the top and bottom surfaces. As mentioned in section 6.2 this waviness causes optical scattering which increases the propagation losses of light across the suspended waveguide; this roughness would also increase the intrinsic losses of a microresonator. Therefore, it is imperative that the waveguide's surface roughness is minimum. Three different methodologies are known to decrease the roughness of microstructures fabricated in fused silica: thermal annealing [128], CO₂ laser irradiation [57, 61] and exposure to an oxyhydrogen flame [126]. In all these methods the fused silica substrate is heated to a temperature above its strain point, usually between 900°C and 1100°C, which is defined as the temperature at which the viscosity decreases to $10^{14.5}$ poises. At these temperatures, surface tension overcomes thermally decreasing viscosity forces leading to material redistribution in an energetically favourable configuration of smaller roughness. According to Mullins [205], this relaxation is driven through a combination of different mass transport mechanisms: viscous flow (only in play for amorphous materials such as

fused silica), evaporation-condensation (in a closed system), volume diffusion and surface diffusion, with recent studies pointing to viscous flow as the dominant effect [206]. On the other hand, chemical treatment has proven to deteriorate the surface quality [207].

Here, the surface roughness was minimized by performing thermal annealing after chemical etching following the procedure described in section 3.1.3. To study how the planar spacing between exposure lines and the annealing temperature affects the surface roughness, five different sets of microfluidic channels were fabricated to test different annealing protocols. Each set contained three microfluidic channels, each written with the optimal exposure parameters: pulse energy of 60 nJ, scanning speed of 3000 $\mu\text{m/s}$, laser polarization perpendicular to the scanning direction and vertical separation of 5 μm . Only the horizontal spacing between exposure lines was changed between channels, in order to observe how it affected the surface roughness. Horizontal gaps (dy) of 3 μm , 4 μm and 5 μm were tested. After writing, the samples were etched simultaneously in hydrofluoric acid for 80 minutes, in order to guarantee uniformity between the different sets after the etching process. Afterwards, each sample was subjected to a thermal annealing procedure at temperatures of 1200°C, 1210°C, 1220°C, 1230°C, 1240°C and 1250°C. The samples were characterized before and after thermal annealing, through visual inspection under an optical microscope and through contact profilometry. To enable perfect contact of the profile stylus with the channel surface, the microfluidic channels were fabricated with length, width and depth of 800 μm , 500 μm and 80 μm , respectively. The surface roughness was determined from a Python script. First, the data points spanning a 35 μm long region near the channel border were discarded from analysis, as they correspond to a higher error domain due to poor contact between the profile stylus and the channel surface. The Fourier transform of the redefined data was then computed, and a bandpass filter was applied to remove the short-wave component (related to measurement noise) and the waviness and nominal form component (related to irregularities with a large amplitude and to macroscopic deviations from the mean line profile, respectively). Given that surface metrology and the ISO standardized norms are not suitable at the nanoscale domain, the surface roughness was determined following the method proposed by Antonio *et al* [208], which considers the cut-off frequencies to be those that minimize skewness. Accordingly, cut-off periods of 1 μm and 10 μm were chosen to remove the short-wave and waviness components, respectively. The inverse Fourier transform of the filtered data is then calculated, from which the surface roughness is obtained. Figure 6.9(a) shows a comparison between the primary profile, as measured through profilometry, and the waviness and roughness spectra. Both the average (R_{avg}) and root-mean square (R_{RMS}) roughness are calculated through the following equations:

$$R_{avg} = \frac{1}{N} \sum_{i=1}^N |z_i| \quad (6.7)$$

$$R_{RMS} = \sqrt{\frac{1}{N} \sum_{i=1}^N z_i^2} \quad (6.8)$$

where z_i is the height deviation from the baseline at point i . The calculation is done

over the entire measurement range (neglecting the transition regions). The average roughness corresponds to the arithmetic average of the absolute values of the profile height deviations from the mean line, while the root-mean square roughness corresponds to the average of the profile height deviations from the mean line. For each microfluidic channel, three scans are performed with the profilometer along a direction transversal to the orientation of the laser-exposure tracks. The roughness is measured for each scan performed, with the final roughness corresponding to the mean average of all scans (for the same channel) whereas the measurement error is determined from the standard deviation.

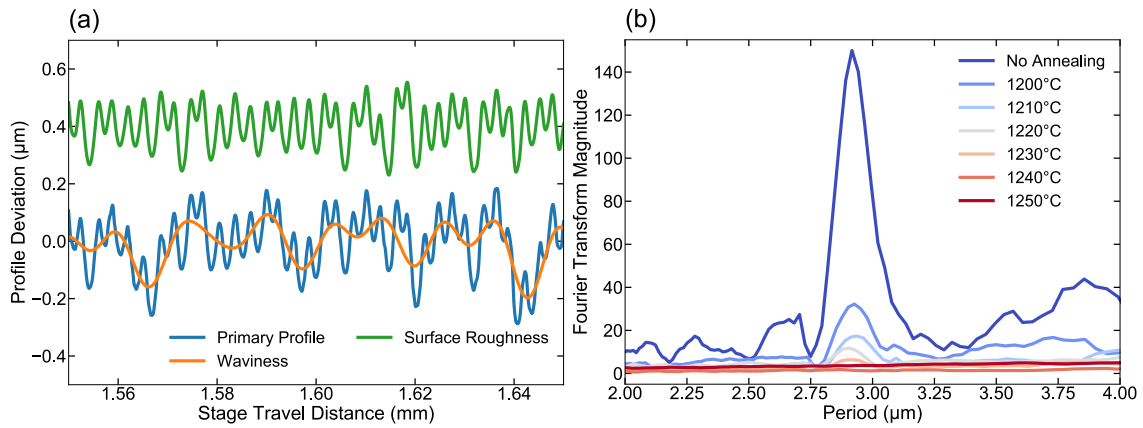


Figure 6.9: (a) Surface topography as measured and after separation of the waviness and roughness profiles after chemical etching of a microfluidic channel fabricated with a planar spacing of 3 μm ; the roughness profile is offset by 0.4 μm to facilitate the analysis. (b) Fourier transform and evolution of the magnitude of the main oscillation with annealing temperature for a microfluidic channel fabricated with a planar spacing of 3 μm .

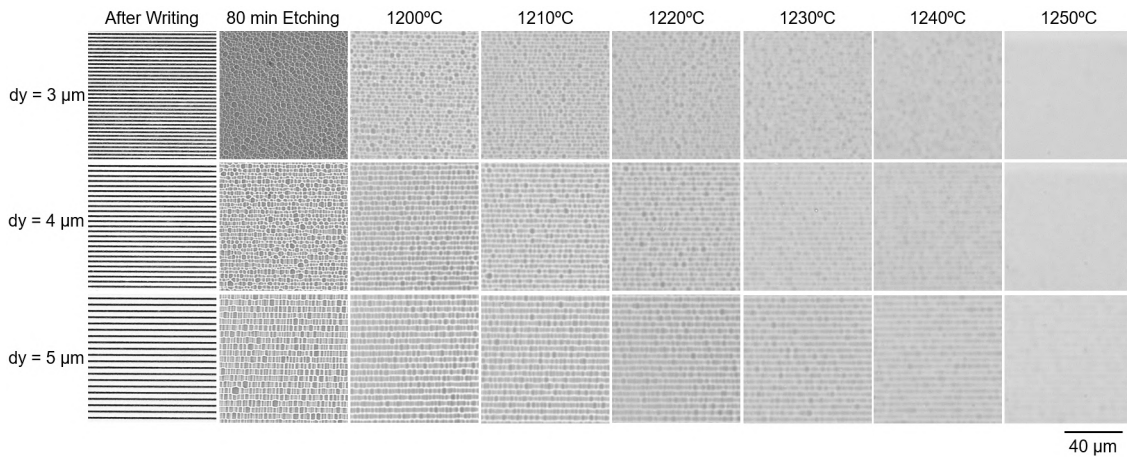


Figure 6.10: Top view image of the microfluidic channel's surface after laser direct writing, chemical etching and thermal annealing at 1200°C, 1210°C, 1220°C, 1230°C, 1240°C and 1250°C, for channels written with planar spacing dy of 3 μm , 4 μm and 5 μm .

Top view images of the surface of the microfluidic channel after laser direct writing, shown in figure 6.10, reveal that the exposure tracks are well-defined, with the centre-to-centre distance between each corresponding to the defined horizontal spacing

dy . After etching, the exposure lines start to merge, thereby forming the microfluidic channel. However, differences in the channel's bottom surface can be seen by varying the gap between the exposure tracks. For dy equal to 3 μm the surface profile looks to be a bit random, whereas for dy equal to 4 μm and 5 μm a preferential alignment direction corresponding to the scanning direction of the exposure tracks is still seen. This point is further driven by computing the Fourier spectrum. In all cases, it is still observed that the channel's bottom surface is periodically modulated, with the dominant period matching the horizontal spacing dy , as shown in figure 6.9(b). However, the magnitude of this peak decreases as dy shortens, proving that the surface is more even when the exposure tracks are written closer to one another. In fact, from figure 6.11, both the R_{avg} and R_{RMS} roughness increase with the separation dy : the average roughness is 72.3 nm, 129.4 nm and 204.6 nm, while the root-mean square roughness is 86.7 nm, 149.2 nm and 229.9 nm for track separations of 3 μm , 4 μm and 5 μm , respectively and right after chemical etching. It should be mentioned that by extending the etching reaction, the surface should become smoother and the roughness should further decrease. The source for the surface roughness is related to the laser direct writing approach, where the chosen exposure parameters lead to a situation where the irradiated tracks are separated from each other by an unexposed irradiated pristine layer. Consequently, when performing chemical etching, these tracks will be etched faster than the pristine material, resulting in an irregular surface profile composed by periodically spaced crests that correspond to the slowly etched layers. This situation is similar to the surface relief pattern observed on the top of the suspended waveguides in figure 6.8. One could ask why gaps lower than 3 μm were not tested as it should conduct to an even lower roughness. In fact, when doing so, cracks start to appear in the channel's bottom surface which is not the desirable situation. Therefore, lower spacings were not tested.

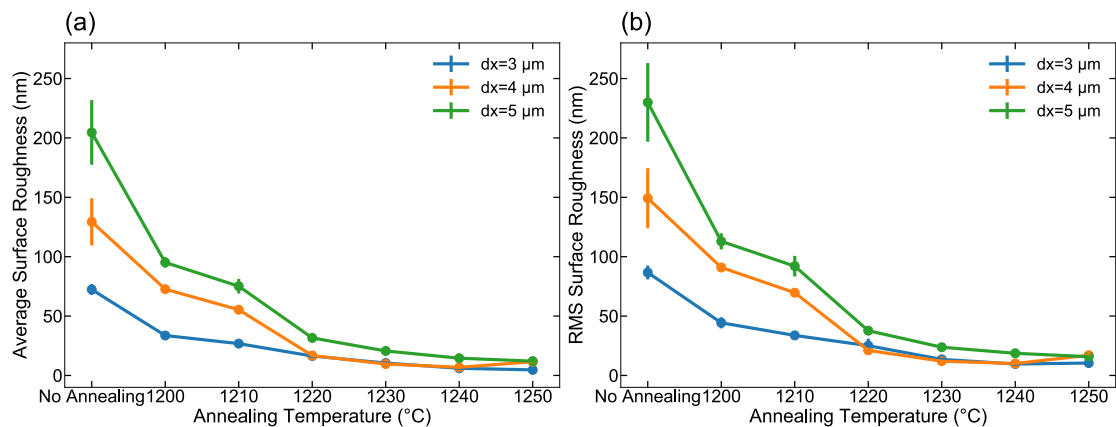


Figure 6.11: Average and RMS roughness of the microfluidic channel's surface after chemical etching and thermal annealing at 1200°C, 1210°C, 1220°C, 1230°C, 1240°C and 1250°C, for channels written with planar spacing dy of 3 μm , 4 μm and 5 μm .

Considering now the surface profiles after thermal annealing, it is noticeable that, regardless of the distance dy , the modulation fades away as the annealing temperature increases. In fact, for a temperature of 1250°C and gap dy of 3 μm and 4 μm , the top

view images in figure 6.10 become completely clear and no topographical contrast is visible. This is also made evident by analysing figure 6.9, which compares the Fourier spectra of the annealed surfaces with the etched one. After etching, the spectrum reveals a dominant peak, centred at a period near the gap dy , whose magnitude declines as the annealing temperature increases. Though these observations are true for all distances dy tested, for a given annealing temperature the modulation is weaker for a lower gap dy . In other words, the channel's bottom surface becomes smoother for higher annealing temperatures and/or for lower distances between the exposure tracks. This is further confirmed when evaluating figure 6.11, which shows the roughness R_{avg} and R_{RMS} for all tested parameters. By performing thermal annealing at 1200°C the surface roughness already decreases by half, relative to the roughness of the surface not subjected to annealing. By increasing the annealing temperature, the roughness continues to decrease, but asymptotically. This behaviour is related to the temperature-dependent material viscosity which, for fused silica, decreases with temperature [209, 210, 211]. The lower the viscosity (higher annealing temperature) the smoother the surface. Similarly, a lower surface roughness is obtained when performing annealing in a wet environment instead of a dry one, because the surface viscosity of the wet sample is lower due to a higher concentration of OH groups [206]. The surface roughness is minimum for an annealing temperature of 1250°C, with the R_{avg} being 4.7 nm, 11.5 nm and 12.1 nm, and the R_{RMS} being 10.5 nm, 17.0 nm and 15.8 nm, for gaps dy of 3 μm , 4 μm and 5 μm , respectively. In comparison, He *et al* [128] observed that the average and root-mean square roughness of the bottom surface of hollow structures made in fused silica substrates (UV grade fused silica JGS1) decreased from 101.5 nm and 120.2 nm to 4.2 nm and 5.2 nm, respectively when annealing at 1200°C for five hours, but with much longer heating and cooling time periods. Other reports also concluded that the surface roughness gradually decreases with the annealing time, before reaching a saturation point [207]; this, however, was not tested here. As mentioned earlier, CO₂ laser irradiation [57, 61] and exposure to hydrogen flame [126] can also be used to decrease the surface roughness. In comparison to thermal annealing, these processes take a few minutes instead of hours and can reach more easily temperatures closer to silica's softening point (around 1700°C) which enable the realization of a lower surface roughness.

From figure 6.11, it is also detected that for a spacing dy of 3 μm and 4 μm , the roughness barely changes for annealing temperatures spanning from 1230°C to 1250°C. This is contrary to what is observed in the top view images of figure 6.10, where a pattern in the surface of the channels annealed at 1230°C and 1240°C emerges, whereas for an annealing temperature of 1250°C the image is completely clear. A possible explanation is that, even though the surface is smooth with no distinct relief pattern, it may present some refractive index inhomogeneities which should explain the observed contrast. To clarify these results, the channels should nevertheless be characterized through atomic force microscopy. The roughness curve also shows that, starting at 1220°C, both the average and root-mean square roughness are equal when writing with a gap dy of either 3 μm or 4 μm . Also, no apparent differences in the top view images exist for channels

annealed at 1250°C, and written with these gaps. Although, all devices presented in this section were written with a separation dy equal to 3 μm , this means that a gap of 4 μm could be used instead, which would decrease the fabrication time without compromising the waveguide roughness after annealing at 1250°C.

Examining now the surface topography of the suspended waveguides, its evolution with the annealing temperature mirrors what was discussed for the microfluidic channel's bottom surface. After chemical etching, a periodic modulation is observed in the top and bottom surface of the waveguide, with the period matching the defined horizontal spacing, whereas a random texture is observed on the channel's sidewalls. As discussed previously, the sidewalls have a lower roughness than the top and bottom surfaces. By performing thermal annealing, the periodic modulation and the relief pattern become less visible, as can be confirmed from figure 6.12. In fact, after annealing at 1250°C the waveguide is completely uniform. Revisiting that the waveguide's surface roughness induces optical losses due to scattering, thermal annealing at 1250°C for five hours is therefore required in order to minimize its propagation losses.

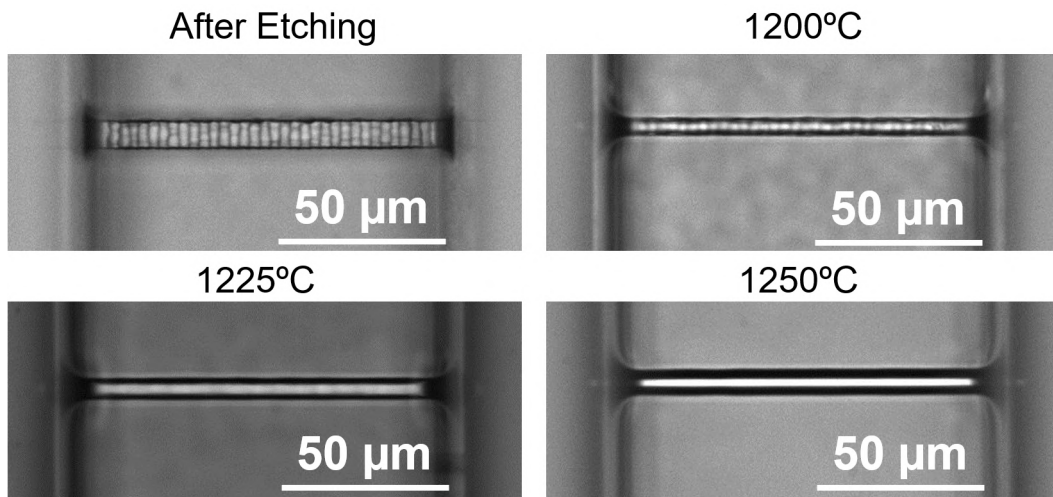


Figure 6.12: Top view images of the suspended waveguide after chemical etching and after thermal annealing at 1200°C, 1225°C and 1250°C. Slightly different etching periods and laser-induced morphing explain the variance in width among the four shown suspended waveguides.

When fused silica is heated to temperatures above its strain point, besides smoothing, surface tension also acts to minimize the surface free energy or, in other words, causes the microstructure to alter its shape in order to minimize its surface area. This morphing mechanism is attractive in microfabrication as it enables the production of circular or spherical-shaped structures with low roughness, which is difficult to realize through direct machining methods. For instance, Drs *et al* [57] demonstrated that a cube sitting on a pedestal turned into a perfect sphere with sub-nanometre roughness, and that a cylinder with a conical cavity in the middle would self-seal after exposure to a CO₂ laser. Here, to understand how thermal annealing affects the suspended waveguide's shape and size, several waveguides of different dimensions (numbered from #1 to #9) were fabricated and subjected to thermal annealing at 1250°C for five hours. Table 6.1 lists

the various combinations of widths and height tested, measured after etching and after thermal annealing. At first glance, it looks like the waveguide's height and width change randomly. However, during annealing, surface tension drives the suspended waveguide to transform itself into a more energetically favourable geometry. In turn, the initially rectangular-shaped waveguide should become elliptical, with the width and height defined in the table now corresponding to the dimensions along the minor and major axis of the ellipse. To confirm this assumption, the cross-sectional area of the waveguide was calculated before and after thermal annealing, with the results being displayed in table 6.1. The cross-section area after etching matches the cross-section after annealing, with a bigger deviation being observed for the asymmetric waveguides (#6 to #9) which could mean that their cross-section resembles more a super-ellipse of order higher than 2. In certain cases, where the width and height are equal after etching, the waveguide acquires a circular cross-section.

#	After Chemical Etching			After Thermal Annealing		
	width (μm)	height (μm)	area (μm^2)	width (μm)	height (μm)	area (μm^2)
1	5.2	6.1	31.7	6.1	6.3	30.1
2	4.8	10.7	51.4	7.8	8.5	52.0
3	4.8	15.5	65.1	8.0	10.0	62.8
4	9.7	5.9	57.2	8.8	8.3	57.4
5	9.4	10.9	102.5	11.1	11.5	100.2
6	9.4	15.8	148.5	12.3	14.4	139.1
7	14.6	5.7	83.2	11.8	9.8	90.8
8	14.8	11.1	164.3	14.5	13.6	154.9
9	14.3	16.2	231.7	16.7	17.0	223.0

Table 6.1: Dimensions of the suspended waveguide after chemical etching with HF acid and after thermal annealing at 1250°C, and respective cross-sectional area. The suspended waveguides are fabricated 30 μm from a polished facet of the substrate to enable imaging of the waveguide's sidewall and measurement of its height. The cross-section after etching corresponds to a rectangle, and after thermal annealing to an ellipse.

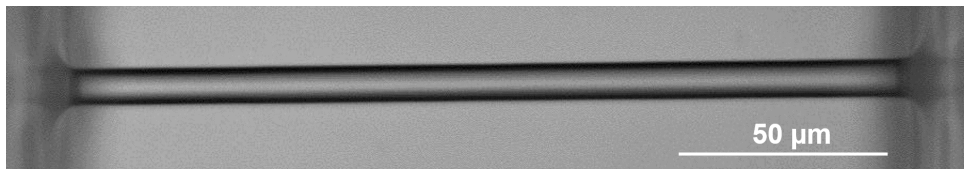


Figure 6.13: Top view image of a 215 μm long circular suspended waveguide with a diameter of 9 μm .

Regardless of the length, the suspended waveguides are stable after etching. After thermal annealing, for lengths shorter than 2000 μm , the waveguide is still uniform throughout its entire length with its boundaries being best described as a short, around 5 μm long, tapered segment, as observed in figure 6.13. However, despite the cross-section dimensions remaining constant, it was observed that the waveguide started to bend downwards for lengths longer than 2000 μm . To understand this, a 5000 μm long

suspended waveguide was fabricated and, after thermal annealing, analysed through optical microscopy. The top view image is not shown here because it cannot be represented in a suitable size while preserving a good enough aspect ratio. After correcting the images for sample unevenness, it was observed that the waveguide bended downwards, being at its minimum near the waveguide's midpoint, before getting back to the initial depth when the other extremity is reached. A maximum vertical downward deviation of roughly $7\text{ }\mu\text{m}$ is measured at its middle point, which translates into a curvature radius of $446 \times 10^3\text{ }\mu\text{m}$ assuming a circular profile. This curvature is not enough to introduce significant optical losses due to bending. However, in some situations where the suspended waveguide's depth is close the channel's one, the waveguide may touch the channel's bottom surface. To attempt to solve this issue, periodically spaced pedestals were fabricated with a square basis with size matching the width of the waveguide, and on which the waveguide would rest. Different periods from $100\text{ }\mu\text{m}$ to $2500\text{ }\mu\text{m}$ were tested, having observed that the waveguide would still bend from its extremity to the first pedestal, but in between pillars it would remain at the same depth. The former feature is explained by the fact that, during annealing, the pedestals start sliding downwards into the channel's bottom surface, thereby causing the suspended waveguide to also drop. Again, the curvature radius of the bended waveguide is higher for longer periods between pedestals. A similar effect was also reported by Cheng *et al* [58], which observed that suspended waveguides fabricated in Foturan glass bended during chemical etching in HF acid. Reasons for this phenomenon were attributed to the fragility of the structure, which is not strong enough to resist to the force generated by the surface tension of the HF acid solution in the ultrasonic bath. They were able to solve this issue by fabricating $100\text{ }\mu\text{m}$ long periodically spaced pedestals, which, nonetheless, introduced an additional optical loss of 0.12 dB per pedestal. In the devices described in the rest of this chapter, the suspended waveguides have a length no longer than $2000\text{ }\mu\text{m}$, so there is no need to fabricate pedestals and this feature can be neglected. Still, other design solutions must be tested in order to fully address this issue.

In the literature, the fabrication of glass suspended waveguides has already been reported in Foturan glass, where these structures are developed to compensate for the incompatibility in fabricating simultaneously optical waveguides and microfluidic channels [58]. Still, the diameter of the suspended waveguides is limited to $20\text{ }\mu\text{m}$ due to the formation of $3\text{-}5\text{ }\mu\text{m}$ long lithium metasilicate crystals which limit the resolution. These structures have also been documented in fused silica, but it is a research topic still underexplored [212]. Similar configurations have also been reported in fused silica and borosilicate glass for optical modulation and switching, which involve laser direct writing of optical waveguides followed by partial removal of the surrounding medium through chemical etching or water-assisted laser ablation [44, 45]. This approach results in a structure composed by a fs-laser written optical waveguide surrounded by a layer of pristine material with typical cross-section size of $50\text{ }\mu\text{m}$, inside a microfluidic channel. Here, much smaller suspended waveguides with diameters around $2\text{-}3\text{ }\mu\text{m}$ can be fabricated. Although the fabrication technique does not impose any limitation on the

diameter of the suspended waveguide, it was observed that smaller waveguides would break more easily during the etching process. An alternative technique to fabricate polymeric suspended waveguides inside a microfluidic channel through self-guiding polymerization is also discussed in annex B.

6.3.2 Waveguiding and Insertion Losses

Having described the fabrication of suspended waveguides in the last section, now it is discussed how light is coupled into the suspended waveguide and how it propagates across it. As is shown in figure 6.3, two fs-laser written waveguides (lead-in and lead-out waveguides) axially aligned with the suspended waveguide are responsible for coupling light into and out of it. Due to the necessity of performing thermal annealing, the lead-in and lead-out waveguides must be fabricated after this procedure. Otherwise, if they are written prior to annealing, they would be erased during thermal treatment at 1250°C. This requirement, however, affects the optical losses of the lead-in and lead-out waveguides. First, the fused silica's topography is far from ideal due to two factors. During the etching reaction, defects in the glass are etched at a different rate and result in a pitted surface; these irregularities prevail even after annealing. Consequently, while writing the lead-in and lead-out waveguides, the fs-laser beam will scan over these pits and be focused at a different depth, thereby creating imperfections in the lead-in/lead-out waveguide which cause scattering of light and increase the propagation losses. Also, during thermal annealing, the sample becomes uneven with both bottom and top surfaces ceasing to be flat. The former leads to some precautions when handling the sample as it hampers its placing over any type of holder (either for laser direct writing or for optical or SEM microscopy), whereas the latter alters the method of writing the waveguides. Because the top surface becomes convex, the sample height needs to be actively modulated while writing the coupling waveguides. Further, when the fs-laser beam scans over the sample's facets, there is a refractive index discontinuity which causes the beam to be focused at two different depths. In turn, near the sample's edge, the waveguide is written with an effective lower energy, which increases the coupling losses. This feature is aggravated by noting that the facets become slightly convex after thermal annealing as well. Both of these issues could be solved if the sample's facets were polished after fs-laser writing of the coupling waveguides. However, this was not attempted as mechanical polishing can easily break the suspended waveguides. All of these issues increase the insertion losses of a single optical waveguide relative to the optimal case, which is defined as laser direct writing over a clean and flat fused silica sample whose facets are polished afterwards. In addition, these features also cause a variance in the insertion losses of similarly fabricated waveguides. Still, these features only affect the optical losses of the coupling waveguides and not those of the suspended waveguide.

The writing method of the lead-in and lead-out waveguides is as follows. After aligning the laser direct writing unit, the sample is placed over its holder and held by vacuum. First, the "Field Calibration" command in the SCA software is executed to align the laser beam focal spot with the camera marker, which will facilitate the alignment between the coupling

and the suspended waveguides. Then, the profile of the microfluidic channel is traced to determine how much it deviates from the stage's axis along the horizontal plane. Knowing this, the coordinate system is transformed to guarantee that the coupling waveguides and the suspended waveguide are parallel to each other. The lead-in and lead-out waveguides are written with a pulse energy of 100 nJ, a translation velocity of 200 $\mu\text{m/s}$ and with the polarization of the laser beam parallel to the scanning direction; as discussed in section 5.2.2 figure 5.5 these parameters ensure that the insertion losses of the coupling waveguides will be minimum in the 1500 to 1600 nm wavelength range. To avoid the "Quill" effect, both are written in the same direction: the lead-in waveguide is written heading into the microfluidic channel, while the lead-out waveguide is written heading away from the channel. To avoid focusing mismatch and energy depletion due to a border effect, the coupling waveguide ends 20 μm from the channel's edge. Still, judging from figure 6.14, this correction is not enough as the waveguide's termination near the walls of the microfluidic channel is slightly blurred; this distance can be decreased if the suspended waveguide is fabricated closer to the surface. This gap is also introduced to avoid ablation and damage of the suspended waveguide's surface when scanning near the channel's edge. Given that after annealing the sample's top surface becomes uneven, the sample's height is modulated during laser direct writing to guarantee that the waveguide's depth is kept constant. This variation is determined by measuring the difference between the position of the Z stage when the laser beam is focused on the surface near the sample's edge and near the channel's edge, and the modulation is synchronous with the translation of the sample across the laser beam. The height correction is different for the lead-in and lead-out waveguides. This procedure is essential as in some cases the height variation can be as high as the depth of the suspended waveguide; consequently, if no correction is done, the laser beam may be focused either at the sample's surface or above it, and the lead-in/lead-out waveguide is not written. Although a linear correction is adopted, which is the easier to implement, this approach is not perfect as the sample's top surface is curved. Consequently, the waveguide's depth slightly fluctuates throughout its length. Still, these variations are smooth which means that there is not a significant increase in the bending loss. In addition, considering the extreme case where the height is deviated by 100 μm along a length of 1 cm, the optical axes of the lead-in/lead-out waveguide and the suspended waveguide are deviated by 0.6° , which means both optical axes can still be considered parallel to each other.

To minimize coupling losses, the optical axes of the lead-in and lead-out waveguides should be aligned with the optical axis of the suspended waveguide. Figure 6.14(f) shows that both are longitudinally aligned if the centre position of the former waveguide matches the midpoint of the latter along the horizontal plane. To guarantee that both waveguides are aligned along the vertical direction, the depth of the lead-in/lead-out waveguide is defined as the depth of the suspended waveguide plus a pre-determined offset of 1 μm . Reasons for this offset will be discussed in detail shortly, but it is related to an uncertainty in determining the centre of the exposure track's cross-section. The depth of the suspended waveguide corresponds to the difference between the Z stage positions between the

sample's surface focus and the waveguide's focus, which are determined through ablation marks and through visual inspection by focusing with the writing objective, respectively. Figure 6.14(a-e) shows top view images of the suspended waveguide focused at different depths, from which it is concluded that the resolution of the visualization setup of the laser direct writing unit along the vertical direction is around 1 μm .

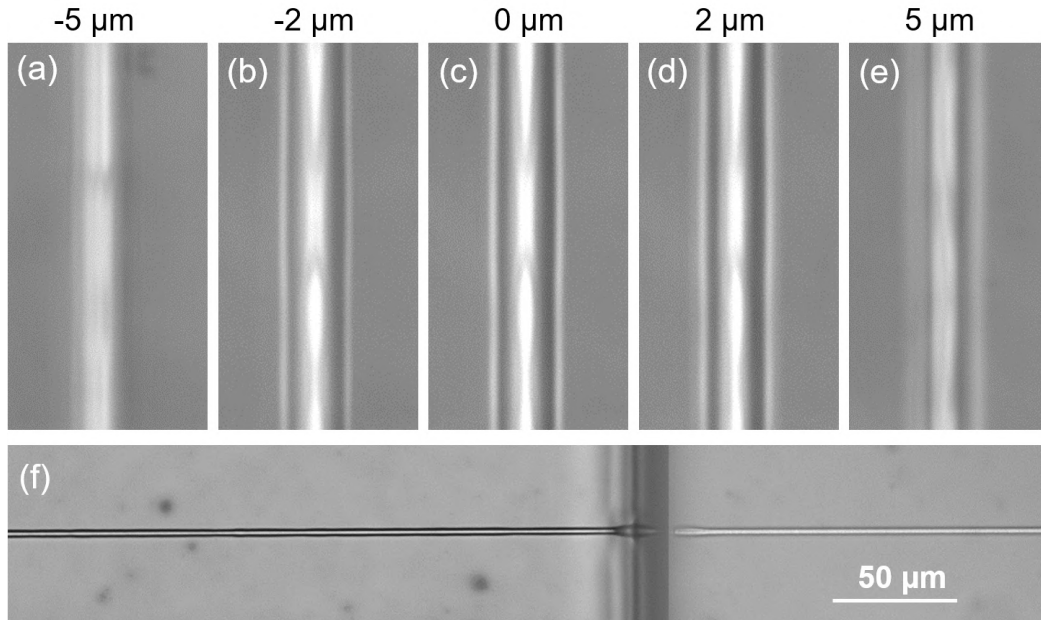


Figure 6.14: Top view images of the suspended waveguide (a-e) at different depths measured relative to the focus of the suspended waveguide and (f) axially aligned with the lead-in waveguide.

All devices presented in this subsection are characterized optically by measuring their broadband insertion losses against different refractive indices of the fluid surrounding the suspended waveguide, according to the procedure described in section 3.2.3. An unpolarized ASE source (EXFO IQ-203 with module IQ-2300) and an optical spectrum analyser (OSA ANDO AQ-6315B) are used as optical source and detector, respectively. The spectra were measured from 1500 nm to 1600 nm with a resolution of 0.1 nm. All the acquired spectra are normalized to the profile losses of the optical source. The measurements were made with the following fluids as cladding: air (empty channel), Cargille Series AA and AAA oil-based fluids $n_D^{25^\circ\text{C}} = 1.3000, 1.3200, 1.3300, 1.3400, 1.3500, 1.3600, 1.3700, 1.3800, 1.3900, 1.4000, 1.4080, 1.4160, 1.4240, 1.4320, 1.4400, 1.4480, 1.4520 \pm 0.002$ and Cargille fused silica index matching liquid $n_D^{25^\circ\text{C}} = 1.4587 \pm 0.0002$ (the Cauchy and Sellmeier coefficients of these fluids are presented in annex A). In between measurements the channel is thoroughly cleaned with isopropanol and deionized water.

First, three microfluidic channels, with respective widths of 504 μm , 1012 μm and 2014 μm , were fabricated, each composed of eleven similarly designed suspended waveguides transversely distanced by 60 μm between each other to prevent coupling. After annealing, the suspended waveguides have a circular cross-section with an average diameter of $6.7 \pm 0.3 \mu\text{m}$. Their length matches the width of the microfluidic channel, and

they are 70 μm beneath the sample's surface (measured to the centre of the suspended waveguide). Each lead-in/lead-out waveguide is written aligned along the horizontal plane with the suspended waveguide, but with a specific vertical offset from its centre. The tested offsets range from -5 μm to +5 μm in steps of 1 μm . A negative offset means that the fs-laser beam was focused at a depth beneath the centre of the suspended waveguide when writing the coupling waveguides, while a positive offset implies the opposite and null offset means the fs-laser beam is focused at the suspended waveguide's depth. The length of each coupling waveguide is between 1.0 cm and 1.2 cm.

The first task is to determine the optimal vertical offset between the coupling and the suspended waveguides that minimizes coupling losses. To simplify this analysis, this study is restricted only to the external refractive indices that guarantee that the suspended waveguide is monomode in the 1500 nm to 1600 nm range. Accordingly, given that the waveguide's diameter is 6.7 μm , only the spectra obtained for the external refractive indices $n_D^{25^\circ\text{C}} = 1.4480$ and $n_D^{25^\circ\text{C}} = 1.4520$ were considered. Measurements made for a waveguide length of 2014 μm were discarded due to the observation of an interference pattern in the transmission spectrum; this pattern will be discussed in detail shortly. Figure 6.15(a) shows the insertion loss profile for the 504 μm wide channel against all vertical offsets tested for an external refractive index of $n_D^{25^\circ\text{C}} = 1.4520$. It is also depicted the insertion losses of a single scan waveguide and the losses of a waveguide intercepting the channel and without a suspended waveguide linking both arms, named "reference" and "w/o bridge", respectively. As can be seen, the insertion losses start to decrease as the vertical offset is reduced from +5 μm to +1 μm , before rising again as the offset is kept shifting downwards. Also, for offsets of -3 μm to -5 μm , the losses decrease with wavelength, mirroring the loss profile for the case where there is no suspended waveguide. This should mean that, for the previous offsets, light is not being coupled into the suspended waveguide and is, instead, propagating unguided across the channel. For the remaining offsets, the losses are constant within the measurement range, similarly to the pattern observed for a single scan waveguide.

Focusing now on the causes for this behaviour, it can be attributed to mainly five different factors: (1) coupling losses between the input/output fiber and the lead-in/lead-out waveguide, respectively, (2) propagation losses across the lead-in and the lead-out waveguides, (3) propagation losses across the suspended waveguide, (4) evanescent absorption of the index matching fluids in the wavelength window tested, and (5) coupling losses between the lead-in/lead-out waveguide and the suspended waveguide.

The insertion losses of the lead-in and lead-out waveguides, factors (1) and (2), should be constant for all devices. However, as explained in the beginning of this subsection, by virtue of fabricating the coupling waveguides after thermal annealing, their insertion losses may vary between devices. Still, this is not enough to explain the behaviour illustrated in figure 6.15(a). Also, regarding factors (3) and (4), scattering losses are expected to be minimal after performing thermal annealing and, according to their datasheet, the absorption of the tested fluids can be neglected at 1550 nm for the tested waveguide

lengths. Consequently, the propagation losses in the suspended waveguide should be almost null. The behaviour observed in figure 6.15(a) is then mainly attributed to the coupling losses between the lead-in/lead-out waveguide and the suspended waveguide, which depend on the assigned vertical offset.

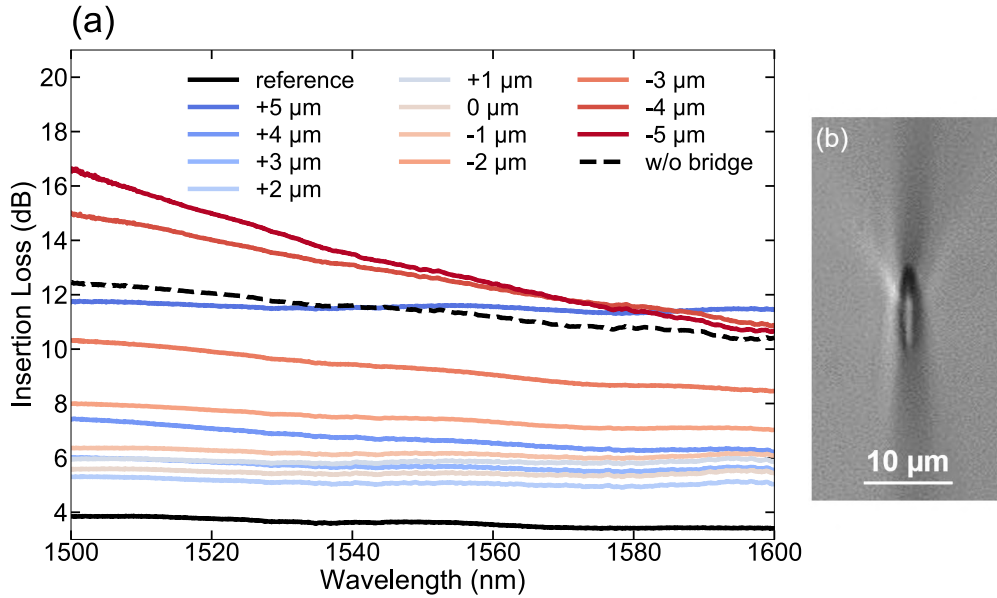


Figure 6.15: (a) Insertion losses of a 504 μm long suspended waveguide with diameter of 6.7 μm surrounded by Cargille $n_D^{25^\circ\text{C}} = 1.4520$, at different vertical offset distances from the lead-in/lead-out waveguide, and (b) cross-section of the lead-in/lead-out waveguide.

To understand this effect, the gathered spectra were normalized to the insertion losses of the respective suspended waveguide when the microfluidic channel is filled with fused silica index matching fluid. This way, the variance of the lead-in/lead-out waveguides' insertion losses can be removed, which facilitates the analysis. Figure 6.16 shows the excess coupling loss at 1550 nm against the vertical offset, after this normalization, for the external refractive indices $n_D^{25^\circ\text{C}} = 1.4480$ and $n_D^{25^\circ\text{C}} = 1.4520$. A symmetric behaviour centred at an offset of +1 μm is observed, which represents the optimal offset when writing the lead-in and the lead-out waveguides for minimizing coupling losses to the suspended waveguide. Also, there is a 3 μm interval where the losses are within 10% of the optimal case, which shows that the margin of fabrication is narrow. The necessity for this offset is related to the cross-section of the lead-in/lead-out waveguide, also shown in Figure 6.15(b). It resembles an ellipse with sizes of 1.7 μm and 13.4 μm along the minor and major axis, respectively. The brighter region is associated to an increase of the refractive index and defines the waveguiding region, whereas the darker zone is associated to a decrease of the refractive index due to the formation of nanogratings. The waveguiding domain has a height of 9.7 μm, which means that the geometrical centre of the waveguiding region is shifted downwards of the exposure track's centre by 1.9 μm. Therefore, a positive offset has to be given when writing the coupling waveguides, in order to shift the centre of the waveguiding region upwards. Still, due to the presence of a layer with refractive index lower than the pristine material, the centre of the waveguiding

region does not coincide with the geometrical centre. This effect, together with eventual non-linear focusing which shifts the laser-modification region upwards, may explain why the optimal offset is closer to 1 μm than 1.9 μm . Although not presented, a similar behaviour was observed for the 1012 μm wide channel.

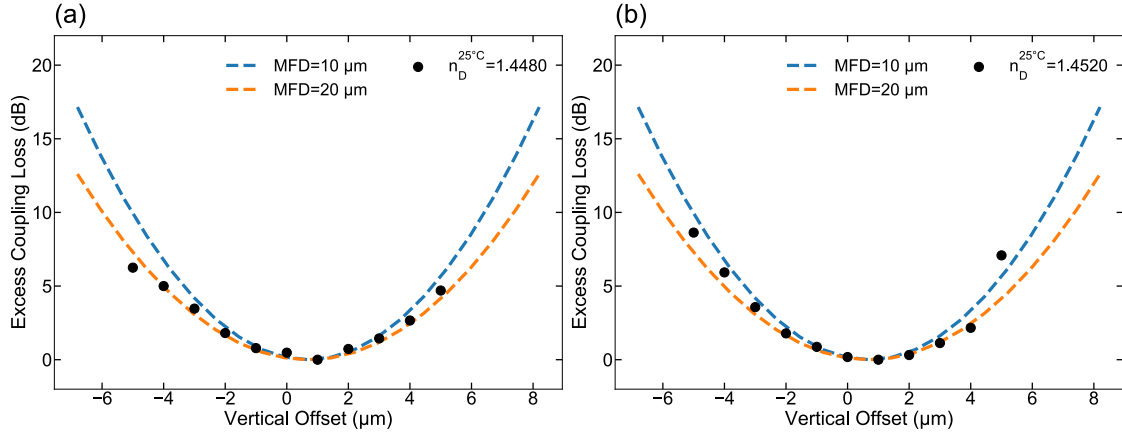


Figure 6.16: Excess coupling losses at 1550 nm of a 504 μm long suspended waveguide with diameter of 6.7 μm surrounded by Cargille series AA (a) $n_D^{25^\circ\text{C}} = 1.4480$ and (b) $n_D^{25^\circ\text{C}} = 1.4520$, at different vertical offset distances from the lead-in/lead-out waveguide. The numerical results were obtained from equation 6.9, where the suspended waveguide was considered circular with a MFD of 10 μm (blue) and 20 μm (orange). Further, the mode field diameters d_x and d_y of the lead-in/lead-out waveguide were considered to be 7.0 μm and 12.5 μm , respectively. The numerical results are horizontally shifted by +1 μm to facilitate the analysis.

Theoretically, the coupling loss depends on mode mismatch and mechanical misalignment between both the lead-in/lead-out waveguide and the suspended waveguide [213]. Losses due to geometrical factors can manifest through angular misalignment, longitudinal separation or lateral displacement. Angular misalignment is caused by the optical axes of both waveguides not being parallel. As discussed above, this deviation is 0.6° utmost, which, in turn, means that coupling losses due to this issue can be ignored. Secondly, the pristine layer in-between waveguides also lowers the coupling efficiency due to an increase of the input waveguide's mode area, as a result of optical divergence, which decreases the common mode area between the mode profiles of the lead-in/lead-out waveguide and the suspended waveguide. Losses due to this factor increase with the longitudinal separation, which means that, ideally, the gap should be null. However, when writing the lead-in and lead out waveguides, the border effect restricts the minimum achievable gap between waveguides, as discussed previously. While this separation can be decreased by writing the suspended waveguides at shallower depths, the depth should still be high enough to avoid damaging the sample's surface while scanning the waveguide. To reach a compromise between both events, the suspended waveguides are written at a depth of 70 μm which determines that the minimum longitudinal separation is 20 μm for the used focusing objective. Lastly, the coupling losses are also affected by introducing a lateral displacement between the optical axes of both waveguides. As discussed previously, this term is the cause

of main concern. As shown in figure 6.14(f), both waveguides are aligned along the horizontal plane, which means that lateral displacement occurs primarily along the vertical direction. From this analysis, and according to the numerical expression determined by Saruwatari *et al* [213], the coupling loss between the lead-in/lead-out waveguide (elliptical shape) and the suspended waveguide (circular shape) is expressed as:

$$CL = 10 \log_{10} \left(\frac{4MFD^2 d_x d_y}{(MFD^2 + d_x^2) \cdot (MFD^2 + d_y^2)} \exp \left[-z_0^2 \frac{2MFD^2 + d_x^2 + d_y^2}{(MFD^2 + d_x^2) \cdot (MFD^2 + d_y^2)} \right] \right) \quad (6.9)$$

where MFD is the mode field diameter of the suspended waveguide, d_x and d_y are the mode field diameters of the lead-in/lead-out waveguide along the horizontal and vertical direction, respectively, and z_0 is the centre-to-centre vertical offset. Figure 6.16 shows how the experimental results compare with the expected excess losses, obtained through equation 6.9 and referenced to the coupling losses at null offset (*i.e.* $z_0 = 0 \mu\text{m}$). Based on previous experiments, the mode field diameters d_x and d_y of the lead-in/lead-out waveguide are $7.0 \mu\text{m}$ and $12.5 \mu\text{m}$, respectively [121]. The mode field diameter of the $6.7 \mu\text{m}$ wide circular suspended waveguide should be between $10 \mu\text{m}$ and $20 \mu\text{m}$ for a refractive index contrast of 0.002 [214]. Figure 6.16 shows that the experimental results agree well with the numerical calculations. It is then concluded that the vertical offset is crucial in minimizing the coupling losses due to mechanical misalignment between the lead-in/lead-out waveguide and the suspended waveguide, and that the optimal scenario occurs by shifting the focusing depth of the lead-in/lead-out waveguides by $+1 \mu\text{m}$ from the suspended waveguide's focal position.

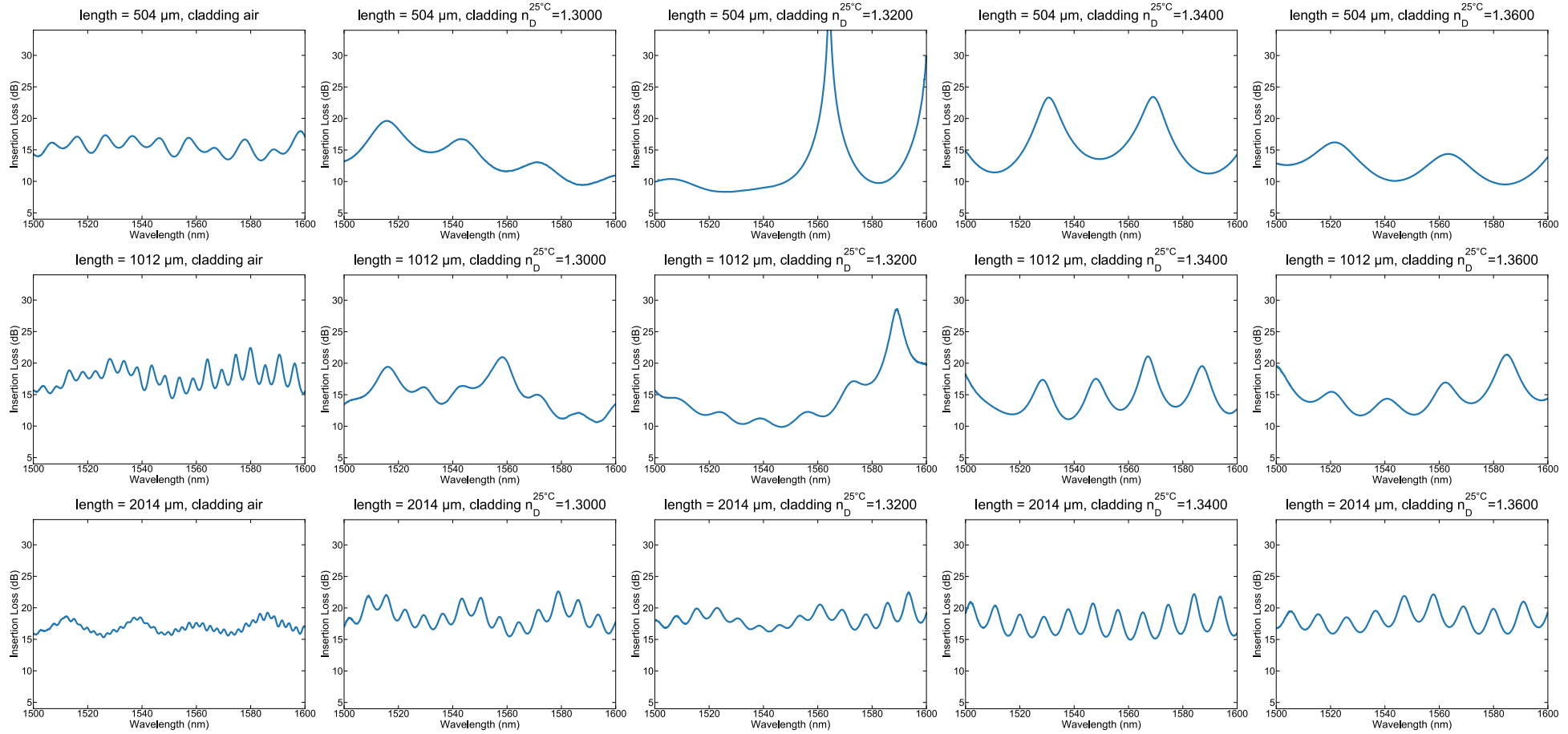


Figure 6.17: Insertion losses of 504 μm (top), 1012 μm (middle) and 2014 μm (bottom) long suspended waveguides with diameter of 6.7 μm with air, Cargille $n_D^{25^\circ\text{C}} = 1.3000$, Cargille $n_D^{25^\circ\text{C}} = 1.3200$, Cargille $n_D^{25^\circ\text{C}} = 1.3400$ and Cargille $n_D^{25^\circ\text{C}} = 1.3600$ as cladding (from left to right).

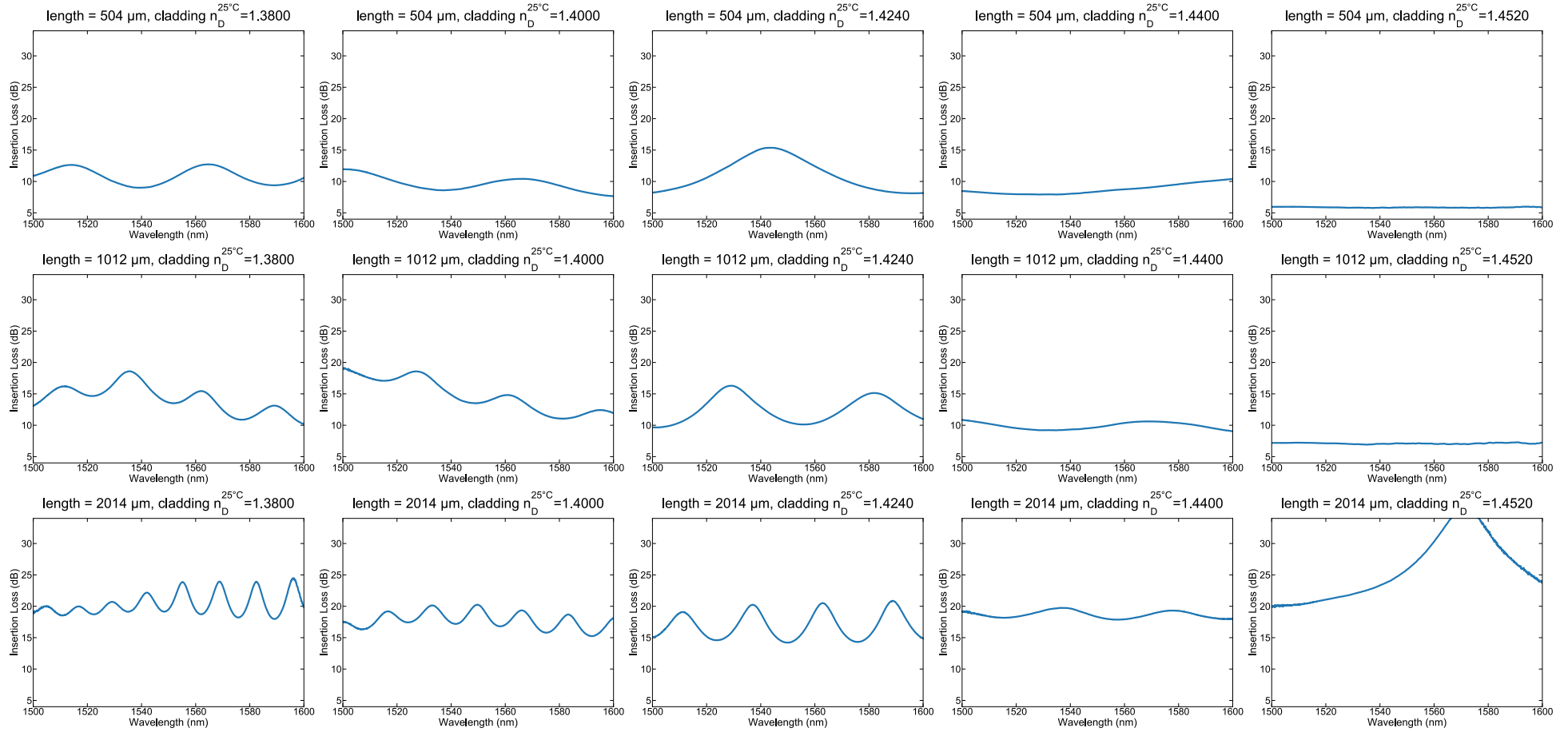


Figure 6.18: Insertion losses of 504 μm (top), 1012 μm (middle) and 2014 μm (bottom) long suspended waveguides with diameter of 6.7 μm with Cargille $n_D^{25^\circ\text{C}} = 1.3800$, Cargille $n_D^{25^\circ\text{C}} = 1.4000$, Cargille $n_D^{25^\circ\text{C}} = 1.4240$, Cargille $n_D^{25^\circ\text{C}} = 1.4400$ and Cargille $n_D^{25^\circ\text{C}} = 1.4520$ as cladding (from left to right).

Figures 6.17 and 6.18 show the insertion loss profile of 504 μm , 1012 μm and 2014 μm long suspended waveguides, with circular cross-section and average diameter of $6.7 \pm 0.3 \mu\text{m}$, against several surrounding fluids of different refractive index. The lead-in and lead-out waveguides are written with a vertical offset of +1 μm from the suspended waveguide to minimize coupling losses due to geometrical misalignment. Unexpectedly, the insertion losses oscillate periodically with the wavelength. The period of oscillation increases as the external refractive index rises towards the fused silica's refractive index, while it lowers for longer suspended waveguides. Additionally, in some cases such as when the channel is empty ($n_{ext} = 1$) and the suspended waveguide is 2014 μm long, this main oscillation is further modulated by a lower frequency wave. On the other hand, for the 504 μm and 1012 μm long waveguide, none of these oscillatory patterns are observed for the external fluids $n_D^{25^\circ\text{C}} = 1.4480$ and $n_D^{25^\circ\text{C}} = 1.4520$, respectively. Instead, in these cases, the losses seem to be constant throughout the entire measurement window.

To understand the insertion loss profile, the characteristic equation of the circular suspended waveguide is solved numerically for all tested fluids. Given that the diameter of the suspended waveguide (6.7 μm) is larger compared to the probe wavelength and the index difference Δ , defined as $\Delta = \frac{n_{core} - n_{cladding}}{n_{core}}$, is smaller than one for all external fluids tested, the analysis is simplified by assuming the suspended waveguide to be weakly guiding. Under these assumptions, the characteristic equations are expressed by

$$V\sqrt{1-b} \frac{J_{l+1}(V\sqrt{1-b})}{J_l(V\sqrt{1-b})} = V\sqrt{b} \frac{K_{l+1}(V\sqrt{b})}{K_l(V\sqrt{b})} \quad (6.10)$$

$$V = \frac{2\pi}{\lambda} \times \frac{d}{2} \times \sqrt{n_{core}^2 - n_{cladding}^2} \quad (6.11)$$

$$b = \frac{N^2 - n_{cladding}^2}{n_{core}^2 - n_{cladding}^2} \quad (6.12)$$

where J_l and K_l are the Bessel functions of the first kind and the modified Bessel functions of the second kind of order l , respectively, V is the generalized frequency, b is the generalized waveguide index, λ is the free space wavelength, d is the diameter of the waveguide, n_{core} and $n_{cladding}$ are the core and cladding refractive indices, respectively, and N is the mode's effective index [215]. Knowing the size and refractive index profile of the suspended waveguide, the V -number can be calculated and used to solve the characteristic equation in order to b (this equation can provide several solutions corresponding to different waveguide modes). This value can be then replaced in equation 6.12 to obtain the effective refractive index of each mode. The suspended waveguide can support the propagation of several linearly polarized LP_{lm} modes, where l pertains to the angular variation of the transverse electric field and m corresponds to the m^{th} root of the waveguide's characteristic equation. The Cauchy and Sellmeier coefficients of all media under discussion can be found in annex A.

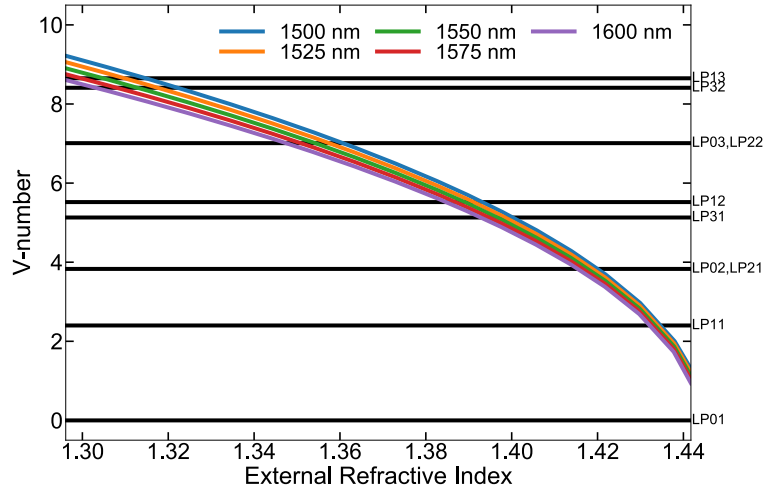


Figure 6.19: Numerical simulations of the V-number, obtained by solving equation 6.11, of a silica-core suspended waveguide with diameter of $6.7 \mu\text{m}$ against the cladding refractive index, for different wavelengths ranging from 1500 nm to 1600 nm. The horizontal lines represent the respective cut-off frequencies of several optical modes, while the refractive index in the x-axis corresponds to the refractive index of the cladding at 1550 nm.

Figure 6.19 shows the generalized frequency V – number against the surrounding refractive index, together with the cut-off frequency of the first nine LP_{lm} modes. To facilitate the analysis, only fluids with external refractive index of at least 1.296 at 1550 nm are considered. The cut-off frequency of the mode LP_{lm} corresponds to m^{th} root of the Bessel function of the first kind $J_{l-1}(V)$ of order $l - 1$; the mode LP_{01} can always propagate across the suspended waveguide. Analysing Figure 6.19, the V-number decreases with increasing wavelength (for the same cladding medium) and with increasing surrounding refractive index (for the same wavelength), as expected. Consequently, at higher wavelengths or with higher cladding refractive indices, the suspended waveguide supports a lower number of LP_{lm} modes and tends to become monomode. The intersection between the V-number and the cut-off frequency curves can be used to determine how many modes are supported by the waveguide at a given wavelength and cladding medium. When the waveguide is surrounded by the Cargille fluids $n_D^{25^\circ\text{C}} = 1.4480$ and $n_D^{25^\circ\text{C}} = 1.4520$, it is monomode throughout the entire measurement range. Given that, with these surrounding liquids, the insertion loss profile still reveals an oscillatory behaviour for a $2014 \mu\text{m}$ long waveguide, it is concluded that the pattern shown in figures 6.17 and 6.18 is not due to multimodal interference. With a cladding composed by liquids of refractive index $n_D^{25^\circ\text{C}} = 1.4320$ and $n_D^{25^\circ\text{C}} = 1.4400$, the suspended waveguide supports two modes LP_{01} and LP_{11} . If the cladding's refractive index continues to decrease towards $n_D^{25^\circ\text{C}} = 1.4000$, the first four modes (LP_{01} , LP_{11} , LP_{02} and LP_{21}) can propagate across the suspended waveguide, and so on and so forth. If the microfluidic channel is empty, the suspended waveguide supports at least nine LP_{lm} modes. Accordingly, from the gathered spectra in figures 6.17 and 6.18, it should be possible to observe a transition delimiting the cut-off of the LP_{lm} mode. However, no transition is observed as not only does the overlapping interference pattern makes this

detection difficult, but it is also unknown how much power (if any) is carried by the higher-order modes.

Knowing the V – number, the effective refractive index profile can be determined after solving the characteristic equation 6.10. Figure 6.20 depicts the effective refractive index profile of the suspended waveguide's fundamental mode LP_{01} and of the LP_{02} mode against wavelength and for all cladding media tested. As illustrated, the effective refractive index of both modes decreases with wavelength and it increases towards the fused silica' refractive index as the surrounding refractive index increases.

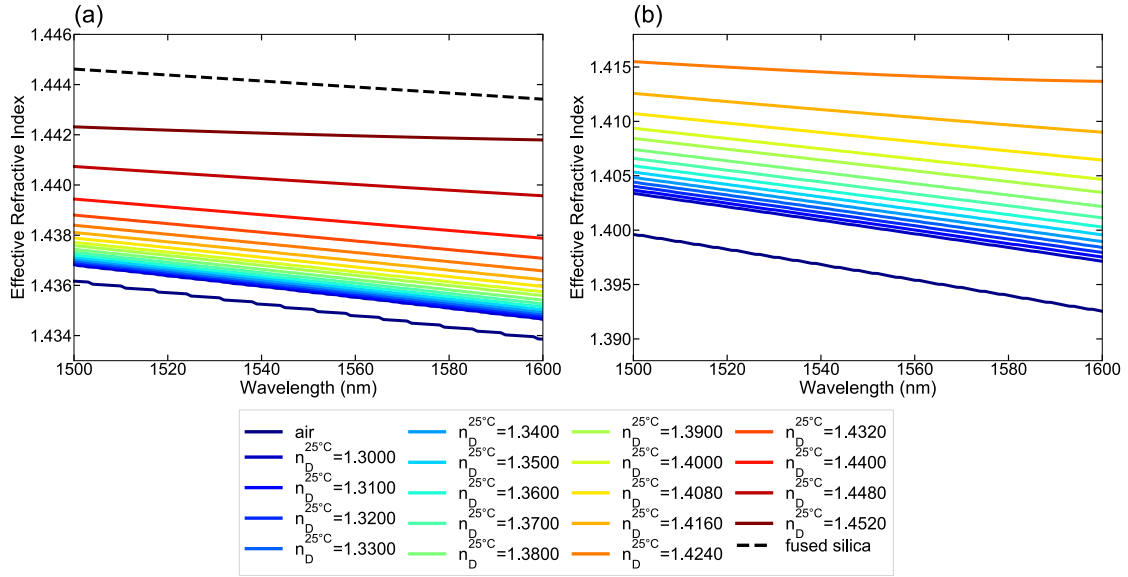


Figure 6.20: Effective refractive index profiles of the (a) LP_{01} and (b) LP_{02} modes of a silica-core suspended waveguide with diameter of $6.7 \mu\text{m}$ against the cladding refractive index. The profiles were determined by numerically solving equations 6.10 to 6.12.

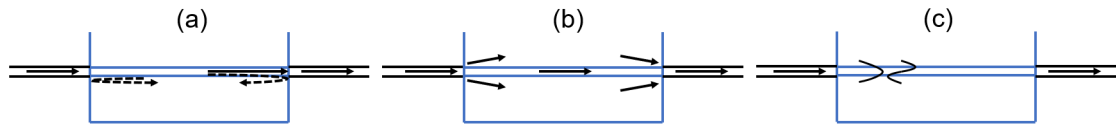


Figure 6.21: Possible interference mechanisms to explain the modulation observed in figures 6.17 and 6.18. (a) Fabry-Pérot interferometer, (b) Mach-Zehnder interferometer between guided modes of the suspended waveguide and unguided light propagating across the microfluidic channel, and (c) modal interference between supported modes of the suspended waveguide.

From the numerical calculations, the origin of the interference pattern can be investigated. The displayed periodic behaviour shown in figures 6.17 and 6.18 suggests optical interference, which can occur due to the existence of a Fabry-Pérot cavity or due to a Mach-Zehnder interferometer. Mach-Zehnder interference can be realized either by interference between light guided along the suspended waveguide and unguided across the channel, or by interference between multiple modes travelling along the suspended waveguide. These phenomena are illustrated in figure 6.21.

First, it is discussed the possible existence of a Fabry-Pérot interferometer, which corresponds to a standing-wave resonator and is formed by an optical cavity bounded by two parallel surfaces. The output spectrum is composed by sharp resonances, located at the wavelengths where the wave transmitted across the cavity interferes constructively with the circulating wave. For normal incidence, the free spectral range ($\Delta\lambda$) and finesse (F) are described, respectively, by:

$$\Delta\lambda = \frac{\lambda_m \lambda_{m+1}}{2nL} \quad (6.13)$$

$$F = \frac{4R}{(1-R)^2} \quad (6.14)$$

where λ_m, λ_{m+1} are the wavelengths of consecutive resonances, n is the cavity's refractive index, and R is the reflectivity at the cavity interfaces for normal incidence. There are three low-finesse Fabry-Pérot cavities in the device. Two of them correspond to the 20 μm long pristine layer (refractive index $n = 1.444$ at 1550 nm) in between the lead-in/lead-out waveguide and the suspended waveguide. If these cavities were to occur, the free spectral range should equal 42 nm and be independent of both the external refractive index and the length of the suspended waveguide. This is contrary to what is observed in figures 6.17 and 6.18, where the period increases with the external refractive index, and decreases as the length of the suspended waveguide increases. The other resonator consists of the suspended waveguide itself, which can occur due to a refractive index mismatch between the effective refractive index of the fundamental mode propagating across the lead-in/lead-out waveguide and the effective refractive index of the modes travelling along the suspended waveguide. Although, from equation 6.13, the resonant period for this cavity is predicted to decrease with the waveguide's length, which matches the experimental observations, the free spectral range should be always below 2 nm which is contrary to the results displayed in figures 6.17 and 6.18. Additionally, for the three cavities discussed, the low refractive index difference between the media forming the cavity does not explain the high fringe contrast observed. For these reasons, the interference pattern displayed in the waveguide's insertion loss profile shown in figures 6.17 and 6.18 cannot be explained through Fabry-Pérot interference.

Another possibility is a Mach-Zehnder interferometer, which is observed when an input light beam is split into two that propagate across different paths, thereby acquiring a phase difference between each other, before being recombined at the output. The transmission spectrum will be composed by sharp peaks located at the wavelength where both beams interfere constructively, *i.e.* where the phase difference is a multiple of 2π . The insertion losses (IL) of a general Mach-Zehnder interferometer can be described through the equation:

$$IL = -10 \log_{10} \left(\frac{1}{2} [1 + \cos(\Delta\phi)] \right) \quad (6.15)$$

$$\Delta\phi = \frac{2\pi}{\lambda} (n_1 L_1 - n_2 L_2) \quad (6.16)$$

where $\Delta\phi$ is the relative phase difference between both beams, λ is the vacuum wavelength, and $n_{1,2}$ and $L_{1,2}$ are the refractive indices and lengths of the path travelled

by each mode, respectively. Two different Mach-Zehnder interferometers can occur as schematized in figure 6.21(b-c).

Figure 6.21(b) shows that one Mach-Zehnder interferometer involves interference between the modes that propagate across the suspended waveguide and light not coupled to the suspended waveguide that propagates unguided across the microfluidic channel. This effect has already been explored in in-line single fiber interferometers, where two single-mode fibers are spliced with a specific lateral offset in order to excite cladding modes of the second fiber, which interfere with each other and interact with the surrounding fluid [216]. Recently, Li *et al* [217] also fabricated a Mach-Zehnder interferometer for temperature sensing, by creating a hollow cavity inside a multimode fiber through fs-laser ablation followed by two-photon polymerization of a 300 μm long suspended waveguide aligned with the core of the fiber. Light propagating through the multimode fiber, upon reaching the cavity, can propagate either through the suspended waveguide or unguided throughout the length of the cavity, with both beams recombining when reaching the cavity's extremity. In that paper, the sensing arm corresponds to the suspended waveguide and the reference arm to the hollow cavity. Here, coupling losses between the lead-in waveguide and the suspended waveguide determine that a fraction of the light coming from the lead-in waveguide is not coupled into the suspended waveguide and, instead, travels unguided across the channel. Because the width of the microfluidic channel is small, the unguided light travels almost parallel to the suspended waveguide and can, therefore, be coupled into the lead-out waveguide. Unguided light travels along a medium with refractive index that is defined by the fluid injected inside the channel, whereas the suspended waveguide supports one or more modes, each with a specific effective refractive index that can be numerically calculated. The physical length of both interfering beams should equal the length of the suspended waveguide (and width of the microfluidic channel). Because the suspended waveguide can support multimode propagation, the full insertion loss profile will correspond to the sum of all of these interferences, where each one is described by equation 6.15. Knowing the effective refractive index of the optical modes propagating across the suspended waveguide and the cladding's refractive index profiles, the free spectral range can be computed and compared with the experimental value measured from the transmission spectra. This way, it is possible to retrieve what waves/modes are involved in the interference process. Although the full insertion loss profile could be calculated instead of comparing free spectral ranges, this approach is more suitable as the power coupled to each mode of the suspended waveguide is unknown.

A Python script was written to retrieve the free spectral range from the measured insertion loss profile. First, it is computed the first derivative of the measured curve in order to the wavelength, and the maxima/minima of each spectrum are determined by checking where the derivative's signal changes from positive/negative to negative/positive, respectively. Because in some cases, it is clear the existence of a low-frequency modulating wave, such as in the spectrum of the 2014 μm long waveguide in an empty microfluidic channel, before computing the derivative, a high-pass filter is

applied to the measured curve in order to remove this modulation. Due to the presence of a high-frequency oscillation in the plot of the first derivative, this function is further filtered with a Savitsky-Golay filter, which is particularly suited for smoothing noisy data. The main idea behind this approach is to make for each point a least-square fit with a polynomial of high order over an odd-sized window centred at the point. The parameters for the fitting window are tuned for each spectrum. Then, the free spectral range is calculated by determining the mean difference between successive maxima and minima. In the cases where the insertion loss profile only shows one maximum and/or one minimum, the free spectral range is estimated as double the difference between the former wavelengths. The obtained results are plotted in figure 6.22 for all lengths of the suspended waveguide tested and against the external refractive index, together with the margins of error.

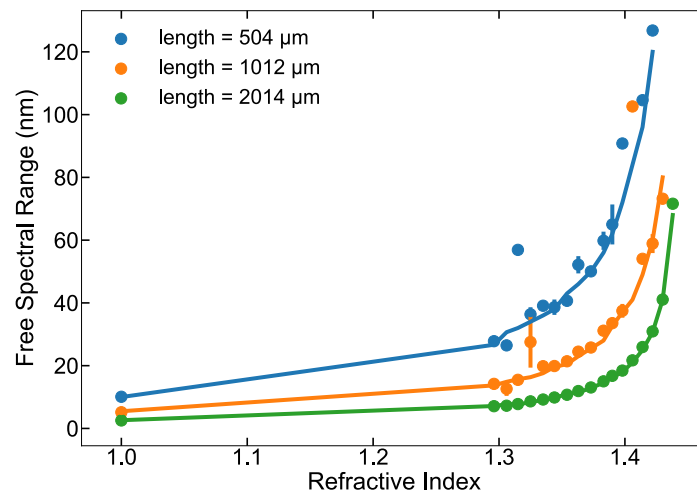


Figure 6.22: Comparison between the experimentally measured free spectral range of the insertion loss profile of figures 6.17 and 6.18 and the numerically calculated free spectral range. The experimental and numerical data are plotted as scatter points and as a continuous line, respectively. The numerical simulations were performed by solving equation 6.15 between the LP_{01} mode of a fused silica-core suspended waveguide with diameter of $6.7 \mu\text{m}$ and unguided light propagating across the microfluidic channel. The refractive index in the x-axis corresponds to the refractive index of the surrounding fluid at 1550 nm .

The free spectral range decreases by a half and by a fourth, as the length of the suspended waveguide doubles and quadruples, respectively. This result is only expected if both arms of the interferometer are physically balanced, which should be the case for the device in question. Additionally, the free spectral range increases non-linearly with the cladding's refractive index, which was again anticipated as, for a balanced interferometer, the period of the modulation is inversely proportional to the refractive index contrast between both arms. Also, in some spectra, even after applying the high-pass filter, other interferences or even mode cut-off can overlap with the filtered spectrum and, consequently, disturb the measurement of the maxima and minima and affect the calculation of the free spectral range. In figure 6.22, these doubtful points with large margin of error can be observed for the $504 \mu\text{m}$ and $1012 \mu\text{m}$ long waveguides. On the other hand, the behaviour for the $2014 \mu\text{m}$ long waveguide is much smoother due to

the existence of a large number of periods within the measurement window, which will decrease these errors. Moreover, when the free spectral range surpasses 50 μm , which is half of the measurement window, the margin of error is higher due to the observation of only one period, or in some cases of only a half-period, in the insertion loss profile.

In spite of the suspended waveguide supporting multimode propagation, the experimental results were compared to the free spectral range predicted by Mach-Zehnder interference between unguided light and the fundamental mode of the suspended waveguide. This is based on studies made for the propagation in tapered fibers. In an adiabatic taper formed in a single-mode fiber, the transition region is smooth enough such that the fundamental mode is unperturbed as it evolves from being core-guided to cladding-guided [191]. In an abrupt taper (non-adiabatic taper transition), although higher-order modes of the same symmetry can be excited, it has been shown that most of the optical power is still confined to the fundamental mode LP_{01} [216]. The expected free spectral range is again determined from a Python script, where after computing the waveguide's effective refractive index for a user-defined waveguide radius and cladding's refractive index profile, equation 6.15 is solved in order to locate the peak wavelengths in between 1500 nm and 1600 nm. The difference between each peak is then calculated to determine the free spectral range. Three simulations were performed, one for each length of the suspended waveguide, where the waveguide diameter was considered to be 6.7 μm and both arms of the interferometer to be balanced with lengths of 504 μm , 1012 μm and 2014 μm , respectively. Figure 6.22 compares the measured results with the theoretical free spectral range, where both curves seem to match well. By computing the Spearman's rank correlation coefficient, to evaluate the correlation between the measured and theoretical values, a correlation of 0.914, 0.946 and 0.998 is obtained for the 504 μm , 1012 μm and 2014 μm long suspended waveguide, respectively. Although the measured trend agrees with the expected behaviour, there are still some slight variations. There is a prevalent mismatch at higher free spectral ranges, which is caused by the low number of periods in the insertion loss profile, as explained before. Additionally, for the 504 μm and 1012 μm long suspended waveguides, some differences at low cladding's refractive index are observed which are attributed to the overlapping interference pattern that affects the measurement free spectral range and explain the poorer correlation.

Still, there is a low-frequency modulation in some of the recorded spectra that has to be accounted for. This additional oscillation is seen in the spectra corresponding to measurements with an empty microfluidic channel, where its free spectral range equals 24 nm and 48 nm for the 2014 μm and 1012 μm long suspended waveguides, respectively. This inverse relation between the free spectral range and the length of the waveguide suggests that these modulations are caused again by Mach-Zehnder interference but between different modes/waves. A subadjacent modulation is also seen in the 2014 μm long waveguide when the cladding is formed by the Cargille fluids with refractive index ranging from $n_D^{25^\circ\text{C}} = 1.3000$ to $n_D^{25^\circ\text{C}} = 1.3200$, where the free spectral range is estimated to be around 35 nm. A modulating wave is also observed for the 1012 μm long waveguide

when the surrounding refractive index is $n_D^{25^\circ\text{C}} = 1.3000$.

The measured free spectral ranges are not comparable to what is predicted if the interference is between unguided light and higher-order modes of the suspended waveguide. Therefore, yet another phenomenon must be occurring. According to figure 6.21(c), another Mach-Zehnder interferometer formed due to interference between the multiple modes propagating across the suspended waveguide can occur. Here, this low-frequency modulation is only observed when the suspended waveguide supports multimode propagation. Given that the lower-frequency modulation is only visible in figures 6.17 and 6.18 for surrounding refractive indices where the suspended waveguide is multimode, modal interference is then a viable mechanism to explain it. Moreover, this phenomenon has already been used to create modal interferometers for refractive index sensing in single-mode – multimode – single-mode fiber configurations [218]. The interference between two modes can again be described by equation 6.15. Therefore, knowing the effective refractive index of each mode, the same procedure can be applied to determine what modes of the suspended waveguide are interfering and causing the low-frequency modulation. After doing this, the closest approximations are obtained for interference between the LP_{01} and LP_{02} modes where, for the empty microfluidic channel, it is predicted a free spectral range of 29 nm, 60 nm and 120 nm for the 2014 μm , 1012 μm and 504 μm long waveguide, respectively. This is further supported by considering that with the lead-in/lead-out waveguide axially aligned with the suspended waveguide only symmetric modes are excited [219]. Moreover, for an abrupt taper, it has been demonstrated that most of the power coupled from the single-mode fiber into the tapered fiber is carried by the LP_{01} and LP_{02} modes [216]. Further, it has been argued that coupling from a single-mode to a multimode fiber mainly excites these two modes since both have similar azimuthal symmetry and the phase mismatch is minimized [220]. Still, the differences between the expected and measured free spectral range need to be clarified. The effective refractive index of each mode were computed considering the weakly guiding approximation instead of solving the full Maxwell equations. This approximation is only valid if the index contrast is lower than one and if the wavelength is lower than the radius of the waveguide. For the cases where the cladding is composed by air and by the Cargille liquid $n_D^{25^\circ\text{C}} = 1.3000$, the index contrast is 30.7% and 10.2%, respectively. In these conditions, the generalized waveguide index b and the effective refractive index are overestimated in the weakly guiding approximation, and the full vectorial solution should be computed instead [221, 222]. This issue is only observed for the low-frequency modulation given that the refractive index contrast between interfering modes is lower for interference between LP_{01} and LP_{02} modes, than for interference between the LP_{01} mode and unguided light.

In conclusion, the periodical behaviour observed in the spectra of figures 6.17 and 6.18 is due to the existence of two Mach-Zehnder interferometers. The high-frequency modulation involves interference between uncoupled light and the fundamental mode LP_{01} of the suspended waveguide, whereas the low-frequency oscillation is only visible in the multimode regime and is due to interference between

the LP_{01} and LP_{02} modes of the suspended waveguide.

Given these results, the previous analysis for the influence of geometrical misalignment on the coupling losses also needs to be revisited. The analysis focused only on the insertion loss profile of the 504 μm and 1012 μm long suspended waveguides, when surrounded by fluids with refractive index $n_D^{25^\circ\text{C}} = 1.4480$ and $n_D^{25^\circ\text{C}} = 1.4520$. Besides the suspended waveguide being monomode in these conditions, only these profiles were studied due to the inexistence of an oscillatory pattern in the output spectra. Still, as just concluded, the transmission spectrum is composed by a periodic pattern formed due to interference between light unguided along the microfluidic channel and the fundamental mode of the suspended waveguide, regardless of the surrounding refractive index. One could then say that the study of the coupling loss is wrong. However, for the refractive indices $n_D^{25^\circ\text{C}} = 1.4480$ and $n_D^{25^\circ\text{C}} = 1.4520$ the free spectral range should be around 800 nm and 2400 nm for the 504 μm long suspended waveguides, and 400 nm and 1200 nm for the 1012 μm long one, respectively. Accordingly, because these periods are much greater than the measurement window, which spans from 1500 nm to 1600 nm, the amplitude of modulation varies very slowly within the measured range and does not influence that analysis.

Similarly to [218], this device could also be used as a Mach-Zehnder interferometer with the suspended waveguide as reference arm and the microfluidic channel as sensing arm. Still, this is not perfect because the effective refractive index of the fundamental mode of the suspended waveguide is also sensitive to variations of the surrounding refractive index as observed in figure 6.20. For a Mach-Zehnder interferometer, the condition for destructive interference, where the insertion loss is minimum, implies the resonances to be centred at:

$$\lambda_{peak} = \frac{2(n_{wvg} - n_{ch})L}{2m + 1} \quad (6.17)$$

$$S = \frac{d\lambda_{peak}}{dn_{ch}} = \frac{2L}{2m + 1} \left(\frac{dn_{wvg}}{dn_{ch}} - 1 \right) \quad (6.18)$$

where n_{wvg} and n_{ch} are the effective refractive index of the fundamental mode of the suspended waveguide and the refractive index of the microfluidic channel, respectively, L equals the length of the suspended waveguide, and m is an integer. Therefore, the sensitivity (S) to the external refractive index only depends on how the effective refractive index of the waveguide's fundamental mode varies with the surrounding fluid. Assuming in first instance that the term (dn_{wvg}/dn_{ch}) weakly varies with the surrounding refractive index, the sensitivity should be around 10000 nm/RIU, which means that the interference peaks should shift by around 100 nm when succeeding fluids with refractive index difference of 0.01 are introduced in the microfluidic channel. Here, given that this equals the size of the measurement window for the spectra shown in figures 6.17 and 6.18, operation of the Mach-Zehnder interferometer as a refractive index sensor cannot be based on the measurement of the spectral shift of the peak wavelengths. To construct a refractive index sensor based on the obtained results, the methodology proposed by Zhang *et al* [223] could be used instead, where the sensitivity to the external refractive index is measured through the variation of the free spectral range.

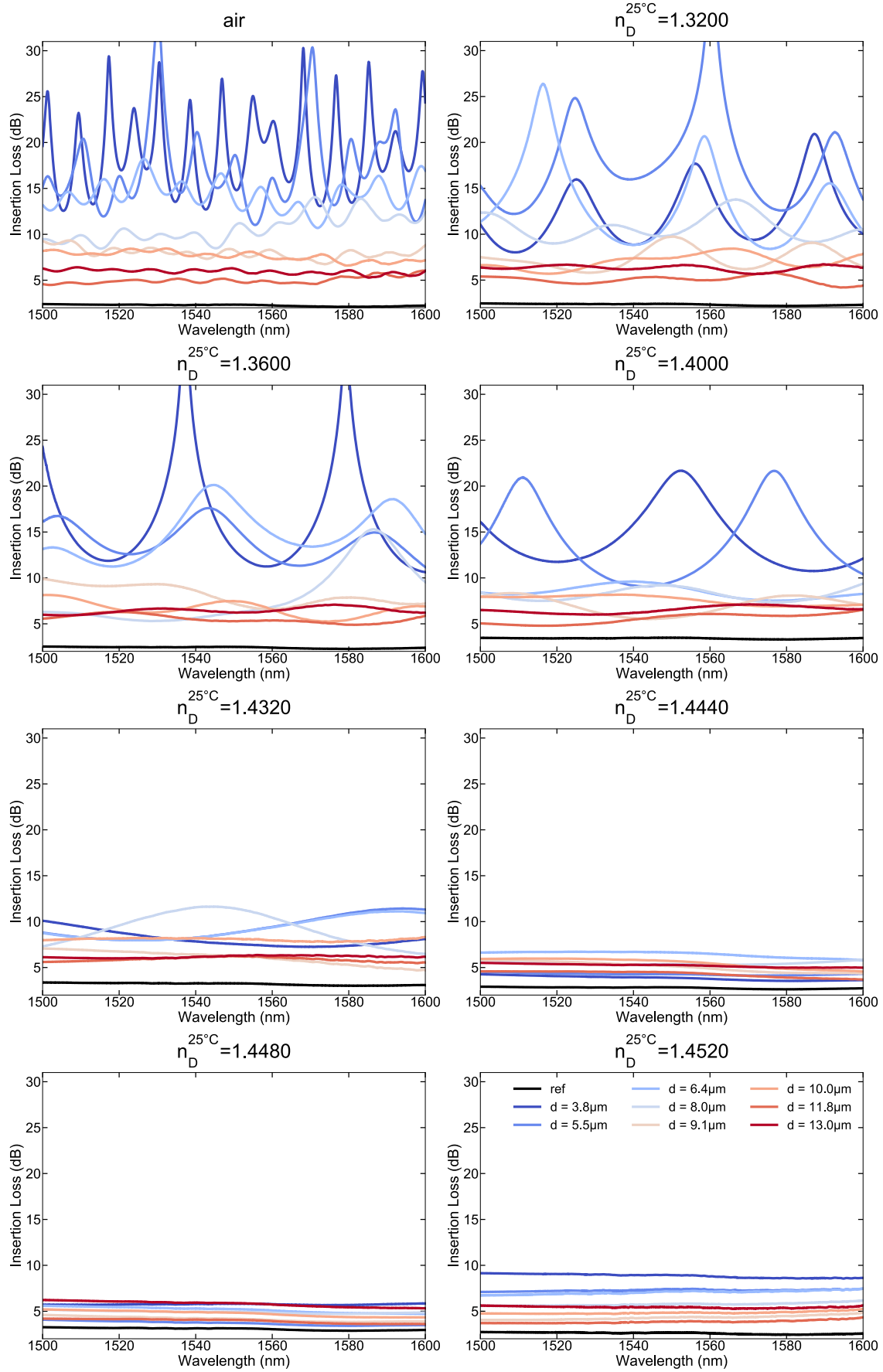


Figure 6.23: Insertion losses of a 492 μm long suspended waveguides with diameters ranging from 3.8 μm to 13.0 μm , with air, Cargille $n_D^{25^\circ\text{C}} = 1.3200$, $n_D^{25^\circ\text{C}} = 1.3600$, $n_D^{25^\circ\text{C}} = 1.4000$, $n_D^{25^\circ\text{C}} = 1.4320$, $n_D^{25^\circ\text{C}} = 1.4440$, $n_D^{25^\circ\text{C}} = 1.4480$ and $n_D^{25^\circ\text{C}} = 1.4520$ as cladding.

Lastly, it was studied how the radius of the suspended waveguide affected its insertion losses. A 492 μm wide microfluidic channel was fabricated, with eight suspended waveguides of circular cross-section and with diameters spanning from 3.8 μm to 13.0 μm (after thermal annealing). The suspended waveguides are buried 75 μm beneath the fused silica surface and are laterally separated by 60 μm to prevent coupling between each other; both of these distances are measured in relation to the centre of the suspended waveguide. The lead-in and lead-out waveguides were fabricated with a vertical offset of +1 μm to minimize coupling losses due to geometrical misalignment, following the procedure described earlier. As an aside, the focus of the wider suspended waveguides is not determined as easily which increases the error associated to vertical misalignment between the lead-in/lead-out and the suspended waveguide. All devices were characterized, as previously described, by measuring the insertion losses from 1500 nm to 1600 nm while varying the refractive index of the fluid surrounding the suspended waveguide. Figure 6.23 shows the insertion loss profile for some specific fluids against the diameter of the suspended waveguide, together with the insertion losses of a straight fs-laser written waveguide that serves as reference.

Again, the output spectra reveals a main modulation caused by interference between the suspended waveguide's fundamental mode LP_{01} and unguided light that propagates across the channel, whose period increases with the cladding's refractive index. However, the fringe contrast depends significantly on the diameter of the waveguide. For instance, looking at the measurements made with an empty channel, a fringe contrast around 10 dB is obtained for a diameter of 3.8 μm which decreases to less than 0.5 dB for a diameter of 11.8 μm or 13.0 μm . For a surrounding refractive index of $n_D^{25^\circ\text{C}} = 1.4320$, a clear oscillation is observed for a diameter of 6.4 μm or lower, whereas the insertion losses are flat throughout the measurement window and equal to the reference ones, minus an offset level, for a diameter of 11.8 μm or higher. This behaviour is again related to the mode profile of the lead-in/lead-out waveguides, which is elliptical with the mode field diameter being equal to 7.0 μm and 12.5 μm along the horizontal and vertical directions, respectively [121]. Consequently, and assuming the optical axes of the lead-in and the suspended waveguide to be parallel, if the diameter of the suspended waveguide is lower than 12.5 μm , a fraction of the light coming from the lead-in waveguide is not coupled into the suspended waveguide and, instead, can travel unguided across the channel. This, in turn, causes the latter to interfere with the modes guided through the suspended waveguide, resulting in the periodic oscillation observed in the insertion loss profile, as discussed above.

The fringe visibility (V) for this interference can be described as:

$$V = \frac{2\sqrt{I_1 I_2}}{I_1 + I_2} \quad (6.19)$$

where I_1 and I_2 are the optical intensities of the mode guided across the suspended waveguide and of the unguided light, respectively. As the radius of the suspended waveguide increases, its cross-section area enlarges and it overlaps more and more with the mode profile of the lead-in waveguide, causing a lower fraction of the optical power to be coupled to the cladding and to travel unguided. Consequently, the decrease in

intensity I_2 lowers the term $2\sqrt{I_1 I_2}$, which defines the amplitude of the modulation, and reduces the fringe visibility and contrast. Therefore, the fringe contrast decreases as the diameter of the suspended waveguide rises, as observed in figure 6.23.

Finally, the coupling losses depend on the mode mismatch between the mode profiles of the lead-in/lead-out waveguide and the suspended waveguide. The mode profile of the suspended waveguide depends on the refractive index contrast and on the radius of the waveguide, which means that the coupling losses can be tuned either by changing the dimensions of the suspended waveguide or by changing the surrounding fluid. For instance, compared to the insertion losses of a reference waveguide, for a cladding liquid Cargille $n_D^{25^\circ\text{C}} = 1.4520$ the minimum coupling losses to the suspended waveguide at 1550 nm are 0.44 dB/facet for a suspended waveguide with diameter of 11.8 μm , for Cargille $n_D^{25^\circ\text{C}} = 1.4480$ as cladding the minimum coupling losses are 0.36 dB/facet for a diameter of 5.5 μm , and for Cargille $n_D^{25^\circ\text{C}} = 1.4440$ as cladding are 0.43 dB/facet for a diameter of 3.8 μm . Although these values also include power that can be coupled to the lead-out waveguide from unguided light, they show that as the refractive index contrast increases, the diameter of the suspended waveguide has to decrease in order for the mode profile of the suspended waveguide to stay constant. Further, the coupling losses can also be tuned by changing the writing parameters of the lead-in and lead-out waveguides.

6.4 Whispering-Gallery Mode Resonators

The goal of this chapter is to fabricate WGM resonators for label-free sensing, following the design depicted in figure 6.3, where the microdisk seats on a cylinder-shaped pedestal with base radius lower than the radius of the microdisk. The evanescent field of light travelling through the suspended waveguide is used to excite whispering gallery modes of the optical resonator. As before, light is coupled into the suspended waveguide from an external fiber, via a fs-laser written waveguide. To construct this device, the design and fabrication process is reviewed to first produce the optical resonators, and then to control the distance between the latter and the waveguide.

Here, a microdisk was used as optical resonator due to its ease of design and high Q-factor. In comparison to other geometries, microrings exhibit lower Q-factors due to the lack of inner rim which increases intrinsic optical losses due to scattering [199, 200]. Further, in fused silica, both microdisk and microtoroids have been already fabricated through fs-laser micromachining and used as WGM resonators by coupling light through the evanescent field of a tapered fiber [60, 61]. Microspheres have also been demonstrated in fused silica by performing CO_2 laser irradiation after chemical etching; however, they have not been used for this application [57].

6.4.1 Fabrication of Microdisks

Akin to the suspended waveguides, the fabrication of the optical resonators starts by laser direct writing, followed by chemical etching and thermal annealing. The writing

design is again composed by vertically spaced layers, which are scanned from bottom to top. Figure 6.24 shows the three different types of layers that will form the device, together with a top view image of the resonator after laser direct writing. The bottom layers include the pedestal structure that supports the microdisk, the middle layers consist of the microdisk itself, while the top layers connect the resonator to the sample's surface similarly to the top layers of the suspended waveguide. Note that although both can be changed at any time, the radius of the pedestal is always lower than the radius of the microdisk.

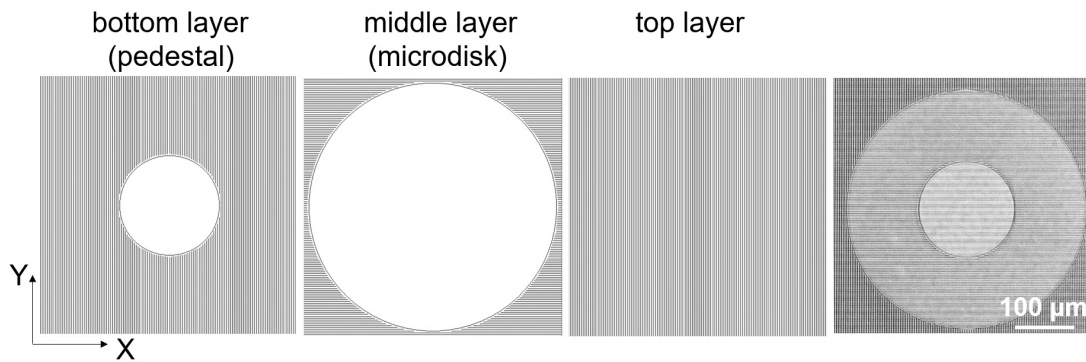


Figure 6.24: Illustration of the three different types of layers used to write a microdisk, together with a top view image of the microdisk after laser direct writing.

In the bottom and middle layers, the laser beam scans first the laser-exposure tracks along the +Y direction and along the +X direction, respectively and according to the reference system of figure 6.24, and afterwards a circle corresponding to the pedestal or microdisk contour, respectively. The laser-exposure tracks are transversally distanced by 3 μm and end 1 μm from the contour. This contour is a single laser scan with a trajectory that follows the edge of the device under construction. Figure 6.25 also shows the importance of writing the disk and pedestal contours. With the contour the lateral wall is smooth, whereas without it there is a sharp transition in-between the exposure tracks that make the microdisk poorly resolved. Because the transversal spacing between exposure lines is kept constant, this transition is sharper for the exposure tracks bounding the top and bottom of the microdisk. In the middle layers, because they will need to include the suspended waveguide (with optical axis along X), the tracks are written parallel to the waveguide axis (X direction) to minimize the waveguide's roughness, as previously explained, and, given that the movement of the translation linear stages is programmed manually, to facilitate the outlining of the irradiation path. This requirement can be neglected in the bottom layers, where the exposure tracks are written along Y to shorten the duration of the laser direct writing process. In both layers, the laser-exposure tracks (with the exception of the pedestal and microdisk contour) are written with the laser beam polarization set perpendicular to the direction of the exposure track. Ideally, the beam polarization should also be orthogonal to the scanning direction when writing the contours in order for the nanogratings to be longitudinal to the scan and to have a minimum wall roughness; however this could not be implemented. Nonetheless, this issue can be

overlooked due to the execution of thermal annealing.

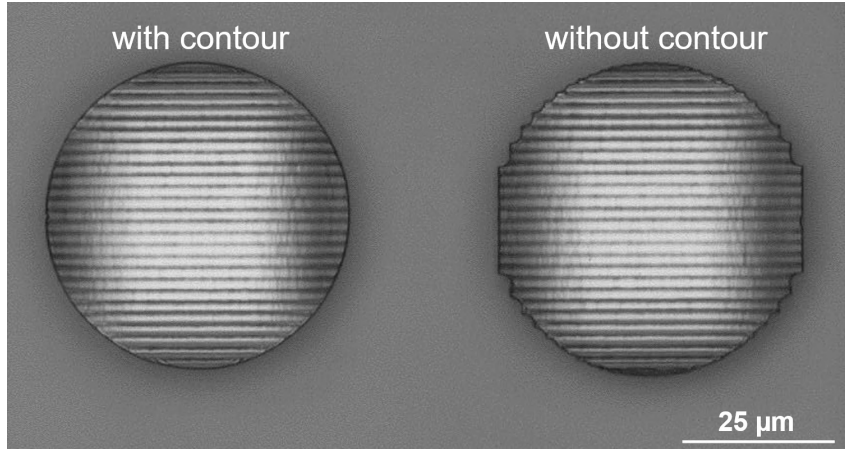


Figure 6.25: Top view image of two microdisk resonators. In the left image the disk contour was written, whereas in the right image no disk contour was laser-scanned, thereby explaining the rougher sidewall.

The top layers are written following the same guidelines applied to the design of the top layers of the suspended waveguides, already described in section 6.3.1. In the middle and top layers, the linear exposure tracks are written with a pulse energy of 60 nJ and scanning speed of 3000 $\mu\text{m/s}$, while in the bottom layer these are written with a slightly higher pulse energy of 80 nJ and scanning speed of 3000 $\mu\text{m/s}$ to speed up the etching process and to guarantee that the pristine material directly beneath the microdisk is removed. Given the close proximity between the exposure tracks and the disk and pedestal borders, the contour tracks are written with a lower pulse energy of 45 nJ and translation velocity of 500 $\mu\text{m/s}$ to prevent stress accumulation and formation of cracks.

The dimensions of the microdisk after laser direct writing and chemical etching evolve similarly to what was discussed for the suspended waveguides. After laser irradiation, the microdisk's radius (r) is related to the designed value (r_{design}) and to the width of a single exposure track (w_{track}), whereas its height (h) depends on the number of layers written (N), the vertical gap between each (dz) and the individual height of an exposure track (h_{track}). Both geometrical parameters are given by the following equations:

$$r = r_{design} - w_{single-track} \quad (6.20)$$

$$h = N \times dz - h_{single-track} \quad (6.21)$$

For the chosen irradiation parameters, the width and height of a single exposure track are 2 μm and 11 μm , respectively. Equations 6.20 and 6.21 are also valid for the pedestal's dimensions. It was measured that during etching, as the HF acid reaches the resonator, the radius of the microdisk start to decrease at a rate of 0.087 $\mu\text{m/min}$ which equals the fused silica etch rate, as expected. However, and unlike the suspended waveguides, the geometry of the microdisk's cross-section slightly changes during etching: the initially vertical sidewall becomes slightly slanted with an average angle of 1°. For microdisk heights ranging from 20 μm to 50 μm , this translates into a radius variation of around 1 μm between the resonator's top and bottom surface. This effect is caused by the

limited etching selectivity, which results in the HF acid starting to etch the disk's top surface before reaching the bottom surface. The higher the disks, the more critical this issue becomes. Figure 6.26 reveals that both the resonator's surface and lateral wall are rugged after chemical etching; akin to the case of a microfluidic channel, the surface topography consists of crests spaced with a period matching the separation between exposure tracks ($3\text{ }\mu\text{m}$), whereas the relief pattern of the sidewall is random and smoother. As discussed in section 6.2, the Q-factor of whispering gallery modes is extremely sensitive to scattering losses and, consequently, to the resonator's roughness, meaning that thermal annealing must be conducted after the etching reaction. Thermal annealing is performed following the protocol established in section 3.1.3, where the sample is heated to at 1250°C and kept at this temperature for five hours. Figure 6.26 also shows the top and side view of the resonator after annealing, where it is concluded that the ruggedness disappears with both the top surface and the sidewall of the resonator becoming smooth. Still, as was in the suspended waveguides, thermal annealing affects the resonator's geometry.

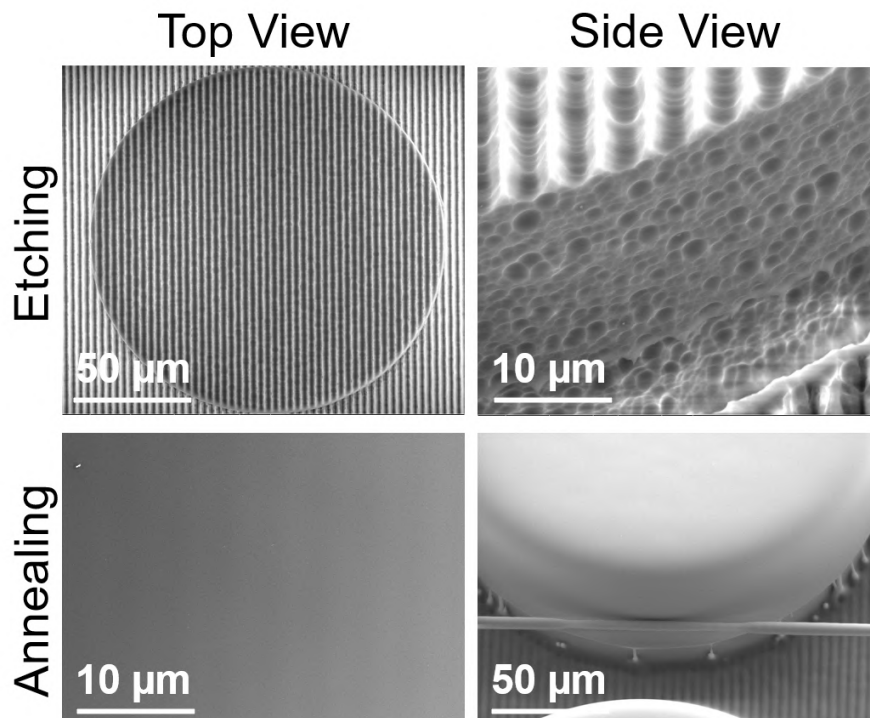


Figure 6.26: Top and side view images, obtained through SEM microscopy, of a microdisk after chemical etching in HF acid for 45 minutes and after thermal annealing at 1250°C for five hours. The side view images were obtained at an oblique angle.

First, to investigate how thermal annealing affects the dimensions of the microdisk, several devices were fabricated, each composed by microdisks of equal radius but with pedestal-to-disk radii ratio varying from 40 to 100% in steps of 10%. Microdisks with radius spanning from $27\text{ }\mu\text{m}$ to $201\text{ }\mu\text{m}$ were tested, with a common height of $25\text{ }\mu\text{m}$. After etching, all microdisks belonging to the same set have the same radius regardless of the pedestal-to-disk radii ratio, as expected. However, as shown in figure 6.27,

the microdisk radius decreases after thermal annealing. The behaviour displayed is transversal to all microdisks tested seeming to depend only on the pedestal-to-microdisk radii ratio. Regardless of the microdisk radius, a minimum decrease of 1-2% is obtained for ratios greater than or equal to 90%. A steady contraction is observed as the pedestal-to-microdisk radii ratio is reduced, with a maximum shrinkage of 7.5% being measured for a ratio of 40%. This shrinkage was also observed by Lin *et al* [60], where it was attributed to surface tension which drives the microdisk to slither thereby causing the microdisk diameter to decrease.

It has been demonstrated that the radius of the pedestal should be lower than the radius of the microdisk to prevent the excited WGMs from leaking to the pedestal [199]. Accordingly, to inhibit coupling of light to the pedestal and to maintain the microresonator's dimensions as close as possible to what was designed, a pedestal-to-disk radii ratio of 90% was used in the following devices. Consequently, for a microdisk designed with radius of 75 μm , the radius of the pedestal is 7.5 μm shorter which should be enough to prevent coupling from the fundamental WGM which is mostly confined to the edge of the microdisk.

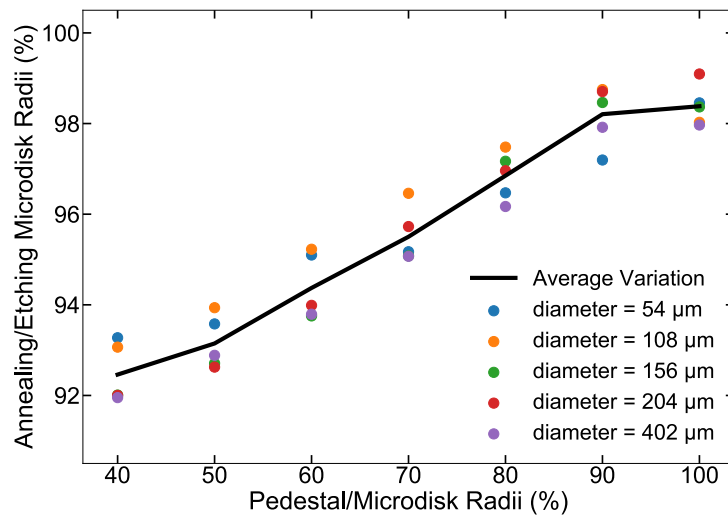


Figure 6.27: Evolution of the microdisk radius during annealing against the initial diameter of the microdisk and against the pedestal-to-microdisk radii ratio.

From there, it was studied how thermal annealing affected the shape of microdisks fabricated with radius and height varying from 50 μm to 150 μm and 20 μm to 50 μm , respectively. Figure 6.28 shows the top and side view images, after etching and after annealing, of the 50 μm radius microdisk. Its geometry, after annealing, depends on the microdisk's height, while it seems to be unaffected by its radius. For all heights tested, the top and bottom edges cease to be straight, becoming round-bevelled. However, while for the 20 μm high disks this causes the sidewall to be completely round, the higher resonators show a straighter section which extends with the disk height. In fact, Song *et al* [61] had already reported that microdisks with heights lower than 20 μm would collapse into a microtoroid due to the action of surface tension, akin to what is observed in figure 6.28. Images taken with lower magnification also reveal that the disk's top surface

is flat. Also, the transition between the microdisk and the pedestal is no longer abrupt, becoming much smoother during annealing, as the material present in the microdisk starts to drain downwards. This also causes the bulges seen in the pedestal sidewall shown in figure 6.26.

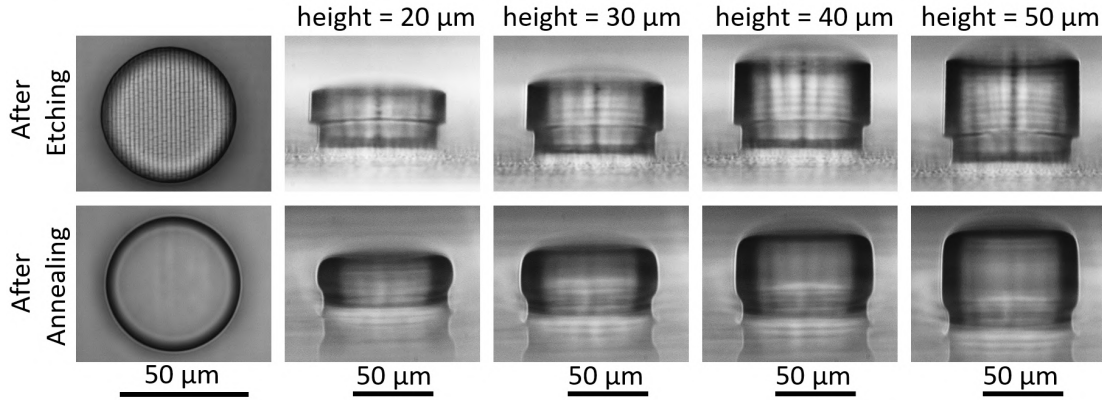


Figure 6.28: Top and side view images, obtained through optical microscopy, of a microdisk resonator with diameter of 50 μm and height varying from 20 μm to 50 μm , after chemical etching in HF acid for 40 minutes and after thermal annealing at 1250°C for five hours.

For excitation of WGMs, the microdisks are designed with a height of 50 μm as it facilitates vertically centring the suspended waveguide in the equatorial plane of the optical resonator. Further, these microresonators possess a straight sidewall (with the exceptions from the round top and bottom edges) which is important to prevent mode splitting or mode superposition usually observed with tilted sidewalls [199].

6.4.2 Coupling between Suspended Waveguides and Microdisk Resonators

In order to excite whispering gallery modes efficiently, several requirements regarding the dimensions of the waveguide and microdisk, and the alignment between both structures need to be met. Revisiting section 6.2, the diameter of the suspended waveguide should be of a few micrometers to enlarge its evanescent field, and it should be placed near the microdisk to promote a larger spatial overlap, thereby increasing the coupling efficiency with the WGMs of the microdisk [191, 204]. As discussed earlier, suspended waveguides with diameter around 2-3 μm can be fabricated, which is close to the typical dimensions of tapered fibers used to excite WGM resonances.

Here, it is discussed the fabrication process to guarantee that both microstructures are aligned with the suspended waveguide tangent to the microdisk. Along the vertical direction, the suspended waveguide is centred in the equatorial plane of the microdisk; this way asymmetric WGMs are not excited [180, 191]. This is implemented during the design of the device, by programming that the layers containing the suspended waveguide fall in the middle of the layers containing the full extent of the microdisk, while offsetting this by the height of a single laser-exposure track. Also, from figure 6.28, the sidewall's

top and bottom edges of the microdisk are round-bevelled with a straight segment in between, which elongates if the disk's height is increased. Therefore, to guarantee that the suspended waveguide is surrounded by a microdisk with straight sidewalls, the resonator is designed with a height of 50 μm . Coincidentally, the higher the microdisk the easier it is to guarantee the alignment between both elements along this direction, at the expense of the microdisk supporting higher-order polar modes.

The biggest challenge is in aligning both structures along the horizontal plane. Here, the suspended waveguide should be nearly tangent to the microdisk, as drafted in figure 6.3, in order to maximize the spatial overlap between the profile of the waveguide's fundamental mode and the excited WGMs. Given that fs-laser direct writing followed by chemical etching is a subtractive technique, implementing this configuration introduces additional difficulties to the design of the device, especially when compared to similar devices fabricated through multiphoton polymerization [67].

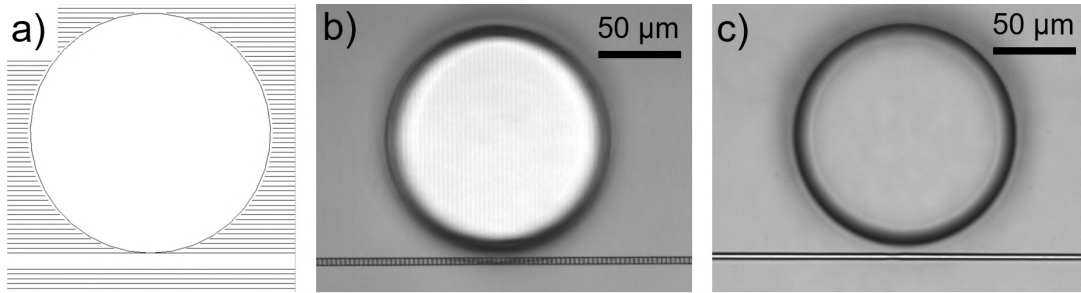


Figure 6.29: (a) First tested design of the WGM microdisk resonator coupled to the suspended waveguide. The waveguide is written tangent to the microdisk, but after chemical etching both structures distance from one another. Image (b) shows a top view image of the device after chemical etching, and image (c) after thermal annealing.

To align both structures along this plane, the first geometry tested corresponded to the exact description provided above, where during laser direct writing the suspended waveguide is already fabricated tangent to the microdisk. Figure 6.29(a) shows the path of the laser exposure tracks in the layers that include the latter structures, making it clear that the laser beam scans the contour of both structures and that the waveguide is written tangent to the microdisk. By writing the contour of the waveguide and the microdisk, the minimum achievable gap is already being limited to the width of a single exposure track, which is around 2 μm , regardless of the etchant used and its selectivity. In addition, during etching, the HF acid will etch into the waveguide and the resonator, due to the finite selectivity, thereby further increasing the lateral distance between both structures. Figure 6.29(b) and (c) also show a top view image of the device after chemical etching and after thermal annealing, respectively, where, at the end, the waveguide is distanced 4.4 μm from the resonator. After writing the lead-in and lead-out waveguides, the output spectrum confirmed that there was no excitation of WGMs. In fact, the spectrum was similar to those of a single suspended waveguide shown in figures 6.17 and 6.18. In all, this design approach cannot be used to excite whispering gallery modes as the gap formed is too large and prevents good spatial overlap between the optical fields of the

waveguide and resonator modes.

The next step was to then change the design in order to pre-compensate the effect of etching unexposed fused silica. A layout of the laser irradiation path is shown in figure 6.30(a). Both structures are designed as a single block, with the suspended waveguide being translated upwards to cross the microdisk, and the intersecting regions being trimmed. The goal is for both structures to be sculpted during the etching reaction, with the etchant causing the suspended waveguide to become thinner and the microdisk shorter, while starting to detach both structures from one another until the waveguide is tangent to the microdisk. However, this situation is never reached as shown in figure 6.30(b), where the HF acid opens a sizeable gap between both structures, which also become deformed. Therefore, when the bridge linking both elements is etched and removed, the device becomes similar to the one shown in figure 6.29 where no WGMs are excited.

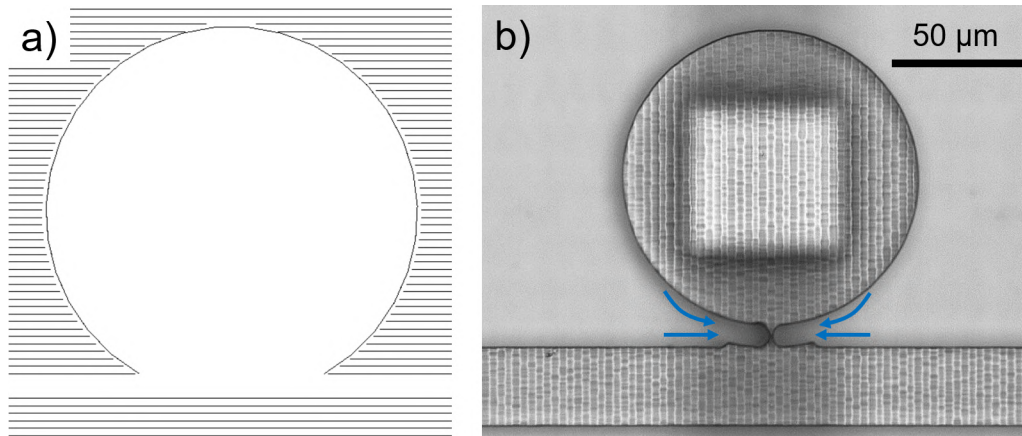


Figure 6.30: (a) Second tested design of the WGM microdisk resonator coupled to the suspended waveguide. (b) Top view image of the device after chemical etching in HF acid. The waveguide is written within the microdisk, but the action of the HF acid causes both structures to separate; the blue arrows indicate the effect of the HF acid within the coupling region.

The design could be further improved by continuously redesigning the microdisk in order to prevent the effects observed during chemical etching. However, by looking to counteract these effects, defining the laser beam path becomes more complicated, which limits what is one of the strengths of the fabrication technique: its design flexibility and control over the dimensions of both microstructures. Instead of trying to control the lateral gap between the suspended waveguide and the microdisk resonator through the chemical etching reaction, thermal annealing was used to morph the suspended waveguide and to place it tangent to the microdisk. The design shown in figure 6.31(a) was tested, where the suspended waveguide is again designed upwards in order to intercept the microdisk, but now with the disk contour being fully drawn. Both structures separate during the etching reaction, with the shape of the suspended waveguide changing in the intersection region: the sidewall of the waveguide's closest to the disk becomes concave while the other one remains straight. However, after thermal annealing, the suspended waveguide centres

itself around its axis, becoming fully symmetric around it and acquiring a taper-like shape. As a result of this transformation, the lateral gap between the waveguide and the microdisk also decreases. If the dimensions of the suspended waveguide are increased and the waveguide is further translated upwards, the lateral gap can decrease to the point where the suspended waveguide is tangent to the disk as shown in figure 6.31(d-e). However, to achieve this, the dimensions of the waveguide are such that the fundamental mode is heavily confined to the waveguide's core and its evanescent field will barely overlap with the WGMs of the optical resonator.

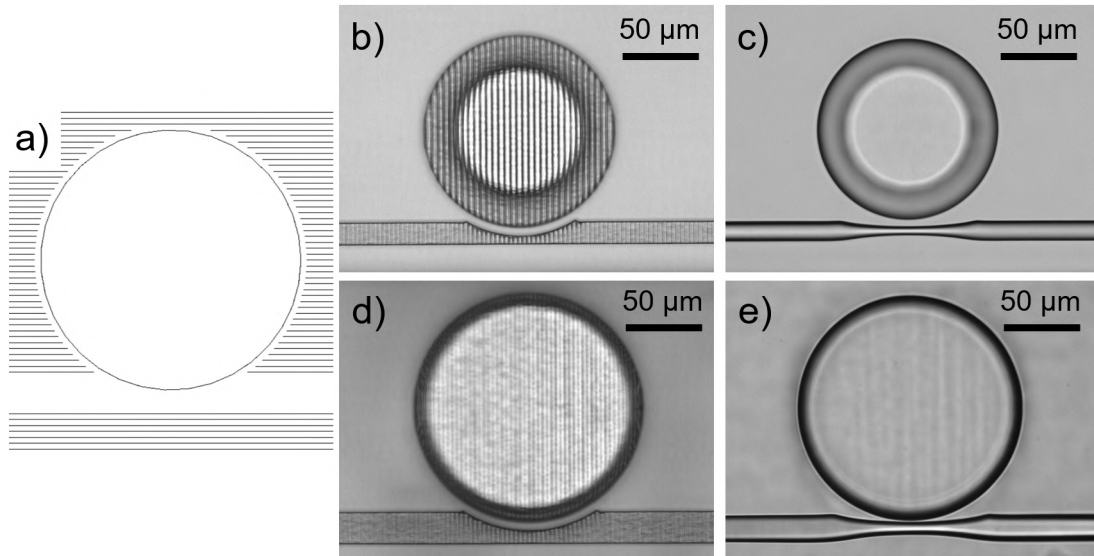


Figure 6.31: (a) Third tested design of the WGM microdisk resonator coupled to the suspended waveguide. The waveguide is again written within the microdisk, but now the contour of the disk is also scanned. (b,d) After chemical etching both structures are separated from one another, but thermal treatment causes the suspended waveguide to realign around its optical axis and to (c) become closer or (e) even tangent to the microdisk.

Therefore, although thermal annealing offers a way to reshape the suspended waveguide and to decrease the lateral gap between the latter and the microdisk resonator, this phenomenon still needs to be observed for shorter waveguides, as these will have an evanescent field large enough to excite WGMs. This, however, requires an overhaul of the waveguide's design. As shown in figure 6.32, the waveguide is now composed by two symmetric straight sections connected by a bended one, whose start and end points coincide with the intersection of the straighter waveguides with the microdisk. The radius of the arc is equal to the curvature radius of the microdisk; although not discussed, it is noted that it is also possible to change the curvature radius of the arc and its start and end points. Figure 6.32(b) illustrates that, during chemical etching, the gap between both structures increases due to the action of the etchant, while the suspended waveguide preserves its shape. However, thermal annealing causes the waveguide to straighten and to recentre around its optical axis, thereby decreasing the lateral gap to the microdisk as shown in figure 6.32(c-d). In figure 6.32(d), it is also demonstrated that the bended waveguide segment can be designed with a lower thickness than the straight

segments, which will cause the suspended waveguide to acquire a taper-like shape within the coupling region. As will be discussed shortly, this control can be used to further decrease the waveguide's beam waist, thereby increasing its evanescent field and spatial overlap with the WGM and facilitating the excitation of WGMs, without compromising the mechanical stability of the suspended waveguide.

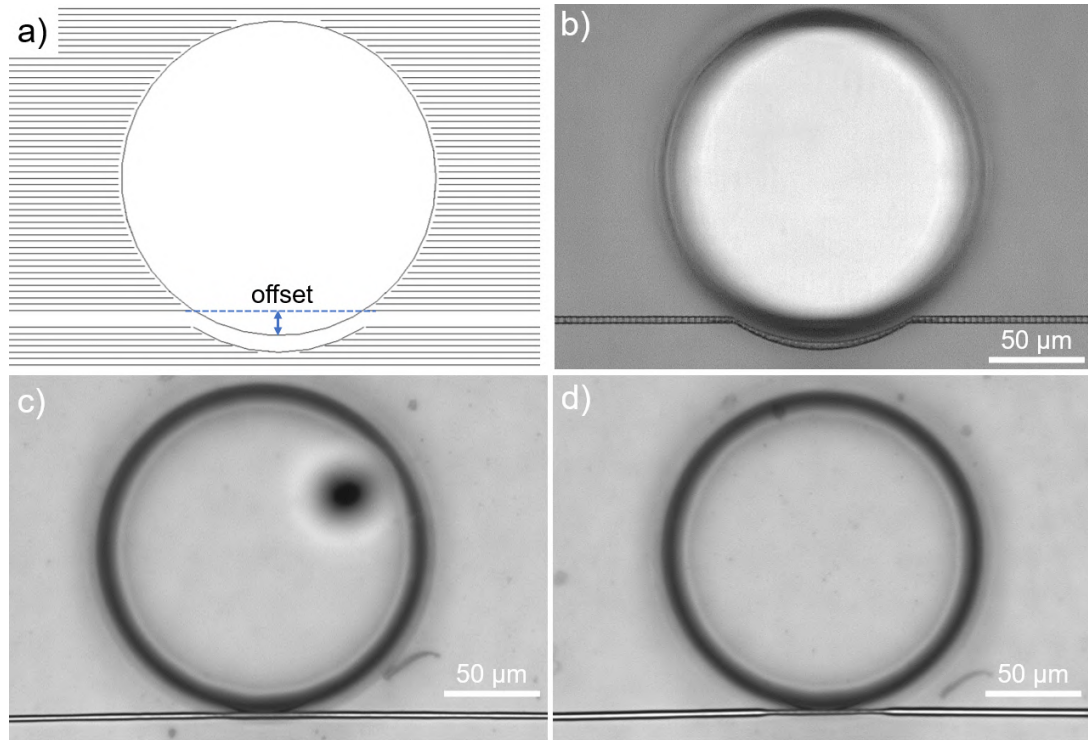


Figure 6.32: (a) Optimized design for excitation of WGMs of a microdisk resonator by the evanescent field of a suspended waveguide. (b) After chemical etching the arc segment of the suspended waveguide surrounds the microdisk, but is separated from it, but (c,d) after thermal annealing the suspended waveguide becomes tangent to the optical resonator depending on the offset defined in (a). The offset corresponds to the distance between the microdisk bottom tangency point and the suspended waveguide upper sidewall. If after etching the offset is null, then after thermal annealing the suspended waveguide is tangent to the microresonator. Figures (c) and (d) also show that the geometry of the suspended waveguide can be tailored within the coupling region by changing the thickness of the arc segment when designing the device; in (c) the waveguide is straight, whereas in (d) it is tapered.

Knowing that thermal annealing causes the diameter of the microdisk to decrease by 2% of its initial value (which translates into a decrease of around 2 μm for a designed diameter of 150 μm) and that the suspended waveguide diameter increases by roughly 1 μm (when morphing into circular shape), the lateral gap between both structures can then be determined during chemical etching. Three different situations, illustrated in figure 6.33, can be obtained which show the control over the position of the suspended waveguide relative to the microdisk, and solely depend on when the chemical etching reaction is stopped. In particular, if the etching reaction is stopped when the straight segment of the suspended waveguide is tangent to the microdisk (null offset according

to figure 6.32(a)) then, after thermal annealing, the arched section will straighten and be tangent to the microresonator, as shown in figure 6.33(b). Figure 6.34 shows a SEM image of the final structure, where the tapered suspended waveguide is straight and tangent to the microdisk, and neither microstructure is deformed in the coupling region. If the reaction is stopped later (negative offset) both structures become distanced as shown in figure 6.33(a), whereas if it is stopped earlier (positive offset) the suspended waveguide merges with the microdisk and becomes deformed as illustrated in figure 6.33(c). In the last case, analysis of the device under SEM microscopy also revealed that, in the coupling region, the suspended waveguide is partially embedded in the microdisk and that it becomes slightly deformed with the outer sidewall turning concave. This depression becomes more visible the higher the offset between the suspended waveguide and the microdisk. This is similar to the observations made by Song *et al* [61], where a tapered fiber would deform when welded via CO₂ laser irradiation to a microdisk resonator, with the original circular cross-section becoming compressed flat-oblate.

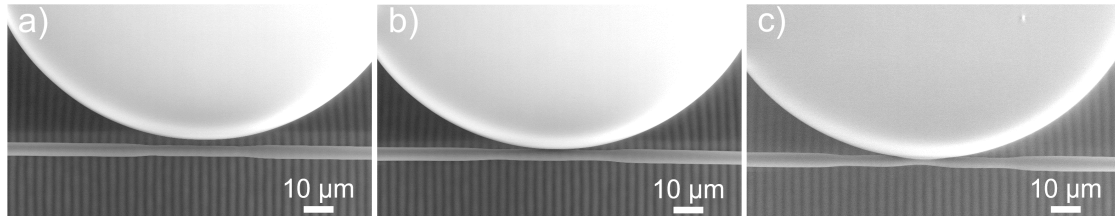


Figure 6.33: SEM images illustrating the possible assembly scenarios: the suspended waveguide is (a) separated from the microdisk, (b) tangent to the microdisk, and (c) merged with the microdisk.

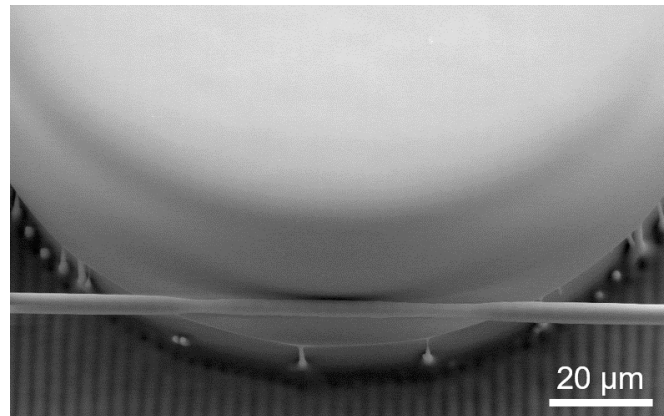


Figure 6.34: SEM image of the suspended waveguide vertically centred with and tangent to the microdisk. The suspended waveguide is tapered within the coupling region, and no deformation is seen in both structures.

Lastly, some minor details regarding the design and fabrication of the device can also impact its geometry. All longitudinal scans begin/terminate one micrometer from the microdisk and suspended waveguide contour to guarantee that the structure, after etching, is a perfect replica of the designed one. If this distance is any bigger, two bulges are observed on the waveguide's sidewalls, after both the etching reaction and thermal

annealing, at the transition from the straighter to the bended section. Further, even after increasing the pulse energy with which the bottom layers are written, the bottom surface of the microfluidic channel has a corrugated profile and the pedestal sidewall presents some defects, as can be observed in figure 6.34. These profiles are a consequence of the finite etching selectivity, and aggravated by the fact that the duration of the etching reaction is determined by the final position of the suspended waveguide relative to the microdisk. As a result, the layers beneath the microdisk are etched for a shorter time period, in comparison to the rest of the material, which translates into a poorer surface quality. Still, these irregularities do not introduce optical losses, and can easily be solved by decreasing the hatching space between laser-exposure tracks in the layers defining the bottom of the microfluidic channel. In some instances, it was also observed that the suspended waveguide would bend downwards and towards the microdisk and/or twist after chemical etching. On some occasions, this was a result of surface tension, and could be solved by heating the sample to around 120°C in order to evaporate remaining liquid in-between both microstructures. These observations may also be related to the fact that suspended waveguide weakens at its entrance and exit, as seen in figure 6.6, thereby becoming more fragile and able to move during ultrasonic agitation. To strengthen it, the waveguide's width was increased by 3 μm over a 10 μm length near the sidewalls of the microfluidic channel, as shown in figure 6.35. Despite observing an abrupt transition after etching, this is converted into a smooth one following thermal annealing.

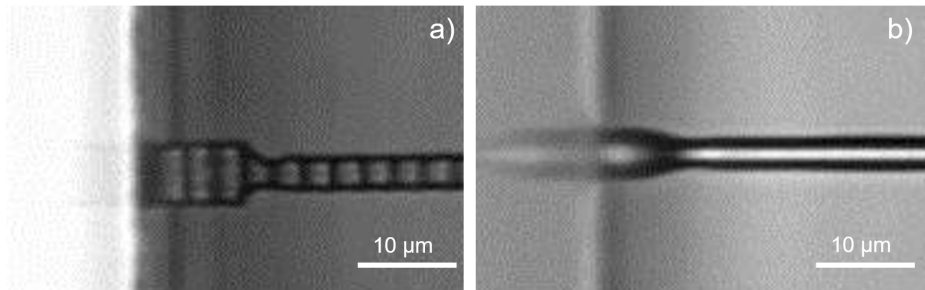
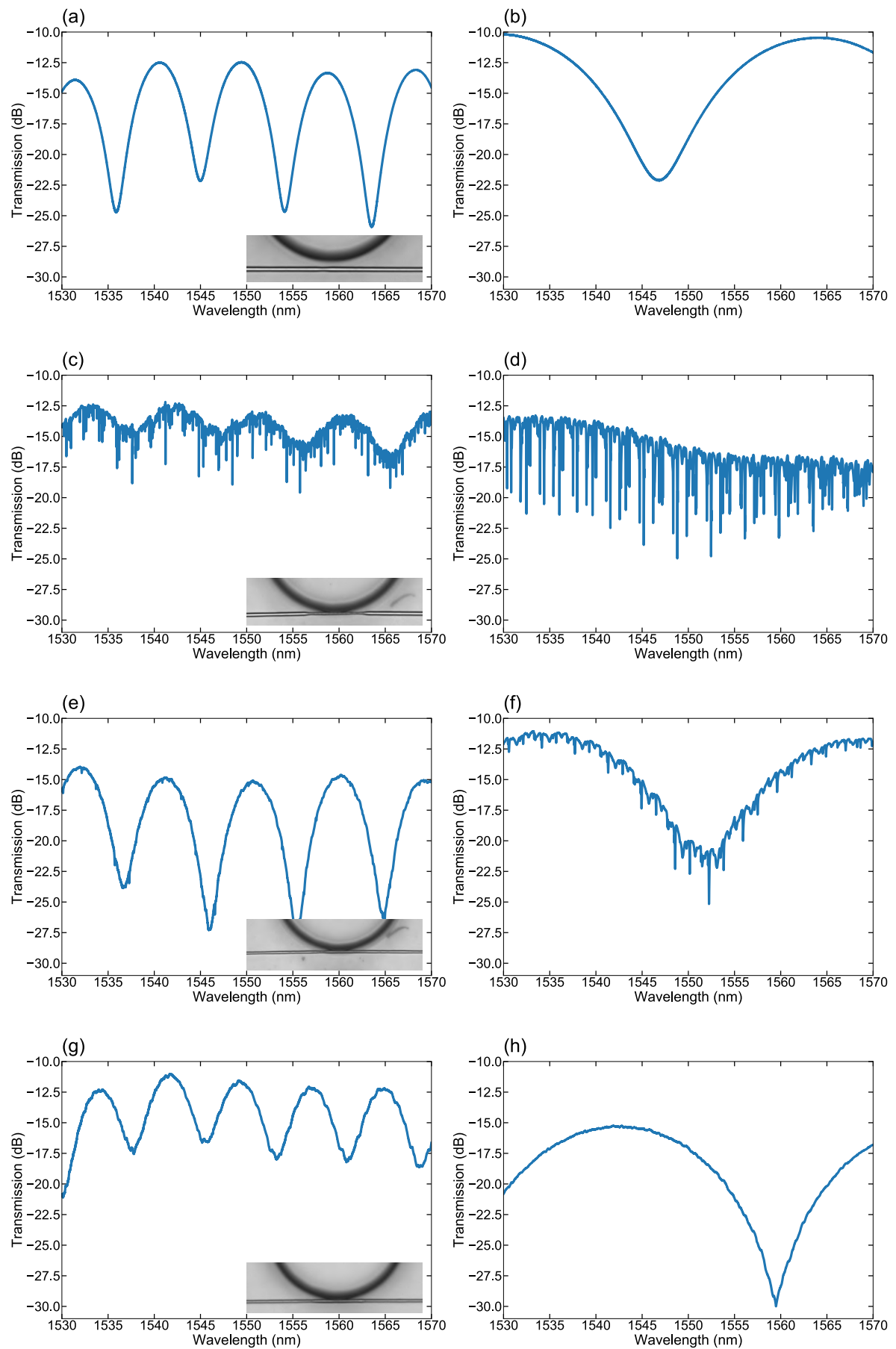


Figure 6.35: Top view images of the suspended waveguide termination (a) after laser direct writing and (b) after chemical etching, showing the added pristine layers that strengthen the anchorage of the suspended waveguide to the sidewall of the microfluidic channel.

6.4.3 Optical Characterization

Following the design and fabrication procedure outlined in the previous section, several devices were fabricated while changing the lateral gap between the suspended waveguide and the microdisk. The resulting transmitted spectrum was measured in air and in deionized water. The measurements were performed with light linearly polarized along an unknown direction, so both TE and TM modes are excited. The microdisk radius and height are 72 μm by 50 μm , respectively. The results are shown in figure 6.36, alongside a top view image of the coupling region.



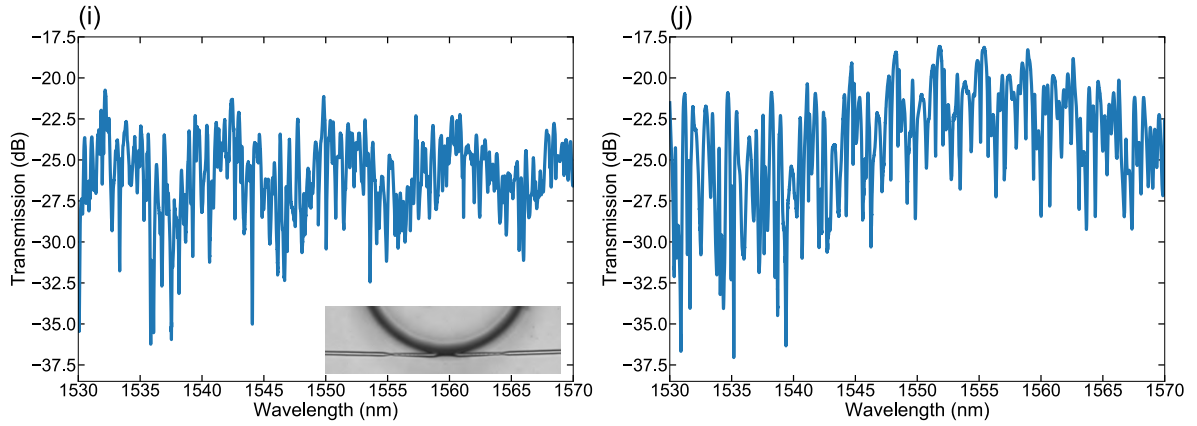


Figure 6.36: Transmission spectrum of a suspended waveguide coupled to a microdisk with radius of $72\ \mu\text{m}$ and height of $50\ \mu\text{m}$ with air (left) and deionized water (right) surrounding the resonator. The inset shows the corresponding configuration.

With a suspended waveguide with diameter of $3.7\ \mu\text{m}$ distanced by $2.2\ \mu\text{m}$ from the microdisk, no WGMs are excited. The transmission spectra, shown in figure 6.36(a-b), is similar to the one obtained for a single suspended waveguide, where the observed periodical pattern is caused by interference between light propagating through the suspended waveguide and light travelling unguided across the microfluidic channel. In this situation, the device is operating well within the under-coupling regime.

With the suspended waveguide tangent to the microdisk, periodically spaced peaks, corresponding to the excitation of whispering gallery modes overlay with this pattern. However, some differences are observed depending on the width of the suspended waveguide within the coupling region. As the diameter of the suspended waveguide in the coupling region increases, WGMs are not as easily excited which translates into a poorer extinction ratio in the transmitted spectrum. With a beam waist diameter of $2.4\ \mu\text{m}$, obtained by decreasing the size of the arched segment of the suspended waveguide relative to the rest of the waveguide, the resonances are easily visible for both media as shown in figures 6.36(c-d). In figures 6.36(e-f), with a straight suspended waveguide with constant diameter of $3.7\ \mu\text{m}$ across its entire length, weak resonances are observed particularly in deionized water due to the larger evanescent field as a result of the lower refractive index contrast. Meanwhile, in figures 6.36(g-h), with a suspended waveguide with a diameter of $4.9\ \mu\text{m}$ within the coupling region and tangent to the microdisk, no WGMs are excited when the substrate is surrounded by either air or deionized water. This stark difference is mainly related to the evanescent field of the suspended waveguide within the interaction region. The evanescent field of the fundamental mode of the suspended waveguide broadens as the core diameter decreases, which leads to a larger spatial overlap and higher coupling efficiency [191].

A completely different spectra is obtained if, after annealing, the suspended waveguide merges with the microdisk, as shown in figures 6.36(i-j). Although the latter is still composed by resonant peaks, these seem to appear in a higher number and to distribute randomly. Only from the measurements made in water, can the periodical

nature of the resonances be discerned. This pattern emerges whenever the suspended waveguide and the microdisk merge during annealing, which is accompanied by the deformation of the suspended waveguide, based on SEM images of the coupling region. This deformation causes several WGMs to be excited which leads to the more complex spectrum, while also increasing the extrinsic losses of the microdisk which reduces its Q-factor. A similar effect was observed by Song *et al* [61] and by Kelemen *et al* [67]. Also, as the waveguide is progressively absorbed by the microdisk, the insertion losses of the suspended waveguide gradually increase. In this situation, the device is operating in the over-coupling regime.

The ideal situation is shown in figures 6.34 and 6.36(c-d), where the extinction ratio is at its highest. Here, the device must also be operating close to the critical coupling condition. In fact, from the results shown in figure 6.36, it is possible to identify the two extreme coupling regimes, under-coupling and over-coupling, and to affirm that the critical coupling condition requires the gap between microstructures to be in-between 0 μm and 2 μm . The whispering gallery mode resonances are periodic, with a spacing of roughly 3.6 nm being measured for both air and water. These values agree well with what is expected theoretically (equation 6.2) if the effective refractive index of the WGM under analysis is considered to be equal to the fused silica's refractive index. The apparent independence of the free spectral range from the surrounding refractive index is associated to a weak variation in the effective refractive index of the excited WGM with the external media. Also, in spite of the WGM spectrum overlapping with the Mach-Zehnder interference pattern described earlier, the period of the interferometric modulation is an order of magnitude higher than the free spectral range of the WGM resonances for all fluids tested. Ergo, the presence of the overlaying modulation does not influence the optical characterization of the WGM resonator.

To better comprehend the results of figure 6.36(c-d), the transmitted spectrum was again measured for this device, but with the input light beam linearly polarized in a known direction. The characterization setup was changed to the one in figure 3.11 to allow measurement of the waveguide's insertion losses with controlled polarization. In the following, 0° and 90° correspond to the polarizations where only TE and TM resonant modes are excited, respectively. Figure 6.37 shows the measured signal when the angle of linear polarization is rotated from 0° to 90°, in steps of 10°. First, in a separate study it was observed that the transmission spectrum of a 500 μm long suspended waveguide (uncoupled from the microdisk) with circular cross-section and diameter equal to 3.7 μm was independent from the polarization direction of a linearly polarized beam. Any changes observed in the transmission spectrum of the optical resonator are therefore related to the excitation of whispering gallery modes. The measurements were made in air and deionized water, having revealed the same behaviour; here, for simplicity only the spectra obtained in deionized water are shown. Initially, with a linear polarization angle of 0°, only the resonant peaks corresponding to TE modes are excited. Zooming in on the peak centred at 1547.8 nm, of figure 6.37, its strength starts to decrease as the angle of polarization is rotated towards 90°, whereas an initially imperceptible resonance located

at 1546.7 nm starts to take form at around 40-50° and reaches its maximum strength at 90°. When the polarization angle is set to 90°, only the TM modes of the resonator are visible. Therefore, rotating the polarization angle allows observation of the transition from excitation of pure TE/TM modes to excitation of pure TM/TE modes. Although not represented, a symmetric behaviour is observed if the polarization angle is rotated to 180°, as expected.

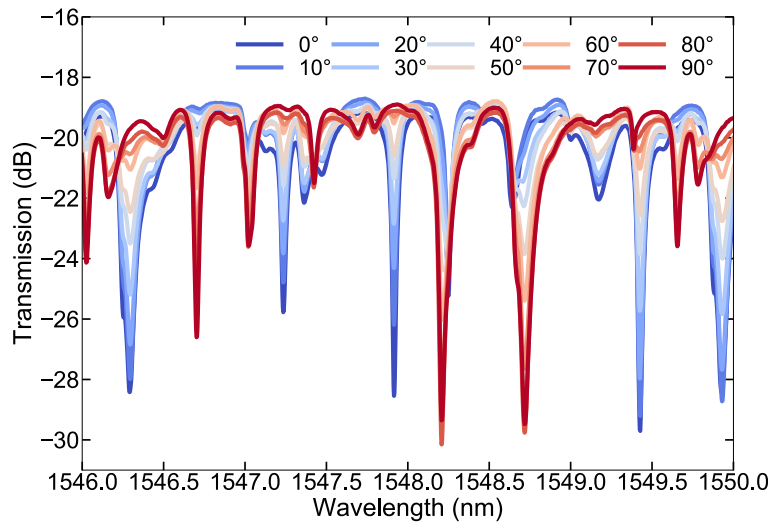


Figure 6.37: Transmission spectrum of a suspended waveguide with beam waist diameter of 2.4 μm tangent to microdisk with radius of 72 μm and height of 50 μm , with the entire microstructure immersed in deionized water, for different input light polarizations varying from 0° to 90°. A polarization angle of 0° means that only TE modes are excited, whereas an angle of 90° means that only TM modes are excited.

Lastly, these measurements were done with an optical interrogator system FS22SA, from HBM Fiber Sensing, where a laser source, continuously sweeping from 1500 nm to 1600 nm with a resolution of 2.5 pm is used to measure the transmitted power. Despite the high resolution, there were some concerns regarding the power measurement operation, which led to some apprehension over the measured spectra. To remove any doubts, these measurements were repeated with a tunable laser (New Focus Tunable Laser Controller TLB-6700 and TLB-6700 Velocity External Cavity Diode Laser) as light source, while the transmitted power was measured in an EXFO Optical System IQ-203 power meter. The exact same spectra as the ones displayed in figure 6.36 was obtained, which validates the measurements made with the optical interrogator system.

To demonstrate its applicability as a refractive index sensor, the device was then characterized against different surrounding media. The sensing principle is based on the interaction between the WGM with the surrounding fluid, where the effective refractive index of the WGM changes with the external refractive index, thereby leading to a spectral shift in the resonant wavelength. Oil-based fluids from Cargille, with refractive index ranging from 1.296 to 1.383 at 1550 nm were used. The device was thoroughly cleaned in-between measurements, and it was confirmed that no contaminants were inside the microfluidic channel nor were they deposited in the surface of either microstructures.

Further, the transmission spectrum of an empty microfluidic channel was measured prior to filling the microfluidic channel with testing fluids, having always obtained a spectrum equal to the reference one shown in figure 6.36(c). This indicates that the device is clean and that the results are repeatable. The measurements were made with light linearly polarized transverse to the microdisk's optical axis in order to excite pure TM modes, and the room temperature was kept at $20 \pm 1^\circ\text{C}$.

Figure 6.38 shows the measured spectra. For all fluids tested, a periodical pattern is observed where all fine features are repeated and the relative peak strength between each resonance is kept constant across all periods. As the external refractive index increases, the number of excited WGMs decreases. This is accompanied by a decrease in the resonance strength and by line broadening, which results in lower Q-factors. These observations can be due to two factors. First, as the external refractive index increases, the number of WGMs supported by the microdisk decreases, similarly to what happens for an optical waveguide [199]. Additionally, the WGMs become less confined and their evanescent field expands. In turn, intrinsic losses due to radiation losses can increase, which result in a lower Q-factor and in a broader resonance [197]. All spectra show a free spectral range around 3.7 nm, regardless of the external refractive index.

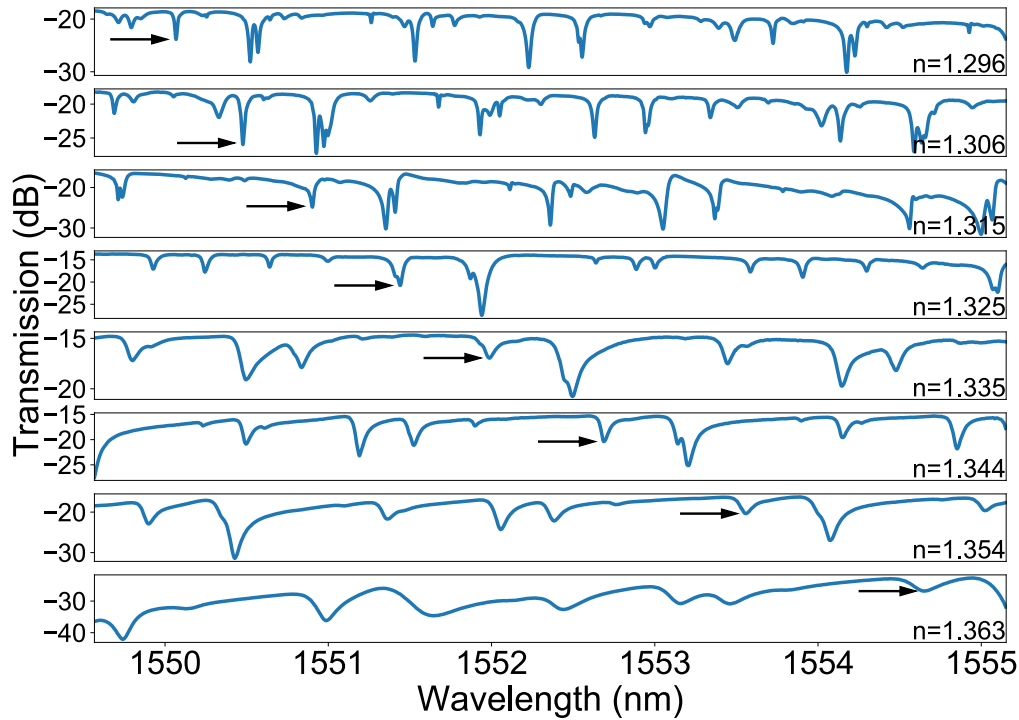


Figure 6.38: Transmission spectra of a suspended waveguide with beam waist diameter of $2.4 \mu\text{m}$ tangent to microdisk with radius of $72 \mu\text{m}$ and height of $50 \mu\text{m}$ against different surrounding refractive indices. Only TM modes are excited. The arrows indicate the WGM under analysis.

To quantify these observations, the behaviour of the resonance located at 1550 nm (marked with an arrow on figure 6.38) was further studied. This analysis was limited to a maximum refractive index of 1.363, as the resonance could not be located at higher

refractive indices. The resonance shifts non-linearly from 1550.068 nm to 1554.652 nm as the surrounding refractive index varies from 1.296 to 1.363. Equation 6.1 is repeated here, which states that the peak wavelength is theoretically described by:

$$\lambda_{res} = \frac{2\pi R}{m} n_{eff} \quad (6.22)$$

where R is the microdisk radius (72 μm), n_{eff} the effective index of the whispering gallery mode, and m is the azimuthal number. Although equation 6.22 states that the resonant wavelength varies linearly with the effective refractive index of the WGM, it does not mean that the variation is also linear with the refractive index of the medium surrounding the microdisk. In fact, FDTD simulations performed by Luo X.-S. *et al* [224] revealed that as the refractive index contrast between the host and surrounding materials decreases, the effective refractive index of the WGM and, consequently the resonant wavelength increased non-linearly, in a similar fashion to the trend displayed in figure 6.39(a). The sensitivity to refractive index corresponds to the first derivative of the peak wavelength curve plotted in figure 6.39(a). Given that the effective refractive index of the WGM does not vary linearly with the surrounding refractive index, it is also expected that the sensitivity varies non-linearly. A maximum sensitivity of 121.5 nm/RIU was obtained at 1.363 with a detection limit of 7.0×10^{-4} [225]. For refractive indices near that of aqueous solutions, the sensitivity is 40 nm/RIU. As mentioned earlier, Kelemen *et al* [67] and Song *et al* [61] also fabricated WGM resonators inside a microfluidic channel, albeit through different methodologies and/or with different materials. In comparison, they reported a linear sensitivity of 61 ± 1 nm/RIU between 1.3344 and 1.3840, and of 220 nm/RIU around the refractive index of water, with a 25 μm radius polymeric microring and with a 40 μm fused silica microtoroid, respectively. Although, the linear sensitivity obtained here is of the same order of magnitude as the one reported for similar configurations, it can still be improved by increasing the interaction between the WGM with the surrounding fluid. This can be accomplished, for instance, by decreasing the radius and height of the microdisk in order to broaden the field of the WGM.

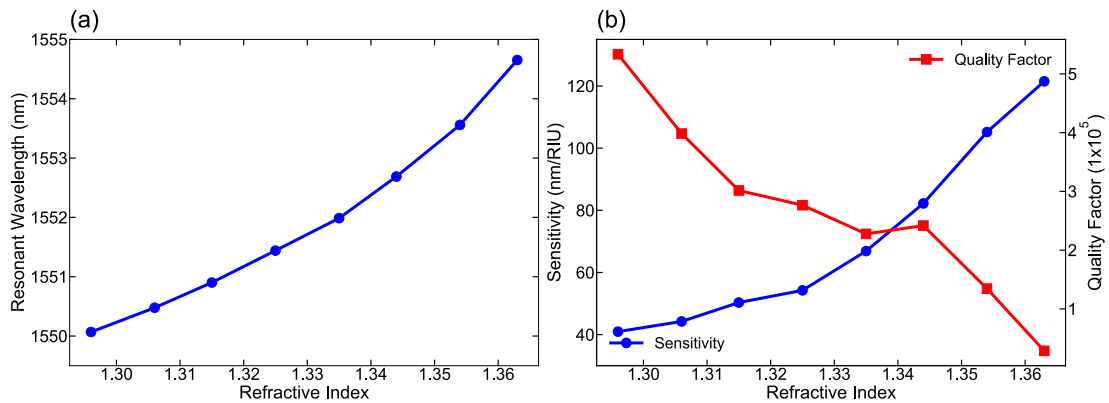


Figure 6.39: (a) Evolution of the resonant wavelength against the surrounding refractive index of the WGM resonator considered in figure 6.38, and (b) respective sensitivity (circular marks) and Q-factor (square marks).

To obtain the Q-factor, the data set pertaining to the analysed resonant peak was

converted into a linear scale, and then fitted with a Lorentzian function ($fit_{Lorentzian}$) given by:

$$fit_{Lorentzian} = A \frac{\sigma}{(\lambda - \lambda_{res})^2 + \sigma^2} - offset \quad (6.23)$$

where the peak wavelength is given by λ_{res} , and the peak width ($\Delta\lambda$), corresponding to the full-width half-maximum, equals two times σ . The peak width is inversely related to the cavity's Q-factor through the equation:

$$Q = \frac{\lambda_{res}}{\Delta\lambda} \quad (6.24)$$

The fitting parameters show that the peak width increases with the external refractive index, which matches the qualitative analysis made previously. This observation is also summarized in figure 6.39(b), where the quality factor reduces from 5.33×10^5 to 0.28×10^5 when the surrounding refractive index increases from 1.296 to 1.363, respectively. This decrease is attributed to weaker light confinement within the microresonator. Notice that, because the spectrum of the whispering gallery modes overlaps an interference pattern, the choice of data points on which to perform the fit is crucial to guarantee the validity of the fitting parameters, in particular the peak width. Still, the obtained Q-factor is enough for most sensing applications. The measured Q-factor is two orders of magnitude higher than what was reported for similar integrated devices with the microresonator surrounded by fluids of equal refractive index [61, 67].

The Q-factor can still be improved by either decreasing the intrinsic or extrinsic losses. In particular, the surface roughness can still be decreased by performing thermal annealing at higher temperatures or for longer periods of time, which would decrease scattering losses [201, 202]. Choosing etchants which remove fused silica at a lower etch rate and with better selectivity than HF acid in a 10% volumetric acid can also be used to provide a more precise control over the dimensions of the suspended waveguide and lateral gap to the microdisk.

Lastly, knowing the free spectral range (f_{sr}) and the resonant wavelength, the azimuthal mode of the WGM under analysis can be estimated according to the equation:

$$m = \frac{\lambda_{res}}{f_{sr}} \quad (6.25)$$

Replacing the measured values in equation 6.25, the azimuthal mode (m) of the analysed WGM is 419.

Two-port WGM Resonator

Ideally, the transmission spectrum should not contain the modulation caused from the Mach-Zehnder interference between unguided light propagating through the channel and the fundamental mode guided through the suspended waveguide, as it may affect the analysis of the whispering gallery resonances. To remove this contribution, the design of the device was changed to the one shown in figure 6.40, where two suspended waveguides are fabricated on each side of the optical resonator and tangent to it. In this configuration, light propagating through the bottom waveguide excites WGMs of the microdisk, which can be coupled into the top waveguide where they counter-propagate

across it. The device can be characterized by either measuring the power transmitted across the bottom waveguide (port 1) or the power counter-propagating across the top waveguide (port 2). Ideally, on-resonance light is entirely coupled into the top waveguide, whereas off-resonance light stays in the bottom waveguide.

The fabrication of the microfluidic channel containing the microdisk and suspended waveguides is similar to what was described previously, with both suspended waveguides being similarly designed. However, the power transmitted through port 2 cannot be measured through a butt-coupled single mode fiber due to spatial limitations from the experimental setup. Instead, a fused silica V-groove block (Precision Micro-Optics) with two parallel SMF28 fibers with a 250 μm pitch between each is connected to the input facet of the fused silica sample. Given that the spacing between the V-groove fibers is larger than the microdisk's diameter (144 μm), the writing method of the lead-in and lead-out waveguides needs to be slightly altered. The bottom suspended waveguide is still linked to straight lead-in and lead-out optical waveguides, whereas the top suspended waveguide is connected to bended lead-in and lead-out waveguides. At the substrate's facet, the respective lead-in/lead-out waveguides of port 2 have to be distanced from those of port 1 by the defined V-groove spacing (250 μm). The lead-in/lead-out waveguides connected to the top waveguide are then composed by three sectors: two straight sections, one connected to a fiber of the V-groove block and other connected to the suspended waveguide, and separated by a bended section composed of two arc-shaped segments that decreases the pitch between coupling waveguides of ports 1 and 2 from 250 μm to 144 μm . The length of the straight sections connected to the substrate's facet is 1 mm to stabilize the mode, and both arc sections have each a length of 2.2 mm and a radius of 50 mm to minimize bending loss [121]; the length of the straight segment connected to the sample's entrance facet is between 4 and 5 mm. Additionally, the stage-controlling software does not allow changing of the sample's height while writing the arc shaped segments, which means that these are written at constant depth. Meanwhile, when writing the two straight sections, the sample's height is varied to compensate for the sample's unevenness, as discussed before.

After fabricating the device, the length of both suspended waveguides is 501 μm and both are tangent to the microdisk, however, in spite of being similarly designed, the diameter of each waveguide is different. The bottom suspended waveguide has a diameter of 3.0 μm from the microdisk, whereas the top waveguide is distanced by 3.4 μm from the resonator. Figure 6.40 shows the transmission spectra of both waveguides when measuring in air and in deionised water. Due to the introduction of the V-groove fibers, the polarization controlling unit cannot be used; consequently the measurements are made with linearly polarized light in an unknown direction. The transmission spectrum at port 1 consists of periodically-spaced resonant peaks that overlap an interference pattern of higher period (as seen before), whereas the spectrum at port 2 is composed by periodical crests placed over a wavelength-independent baseline. As intended, no Mach-Zehnder interference is observed in the output spectrum of port 2, while the resonant wavelengths seem to coincide in both spectra. However, some problems still need to be addressed.

Although the design is fully symmetric, after annealing there are some differences between both suspended waveguides as seen in figure 6.40, regarding their diameter and shape. This asymmetry results in different coupling coefficients between both waveguides which may explain the complex spectrum [192]. We believe that this asymmetry is related to the laser direct writing order, which as shown by Bellouard *et al* [129] will influence the etching dynamics and the morphology of the obtained structures. Here, within each horizontal plane the writing is done sequentially from one extremity to another, but other approaches may be more suitable. Still, it is unclear if this disparity is indeed related to the laser direct writing process or to the chemical etching reaction or to thermal annealing.

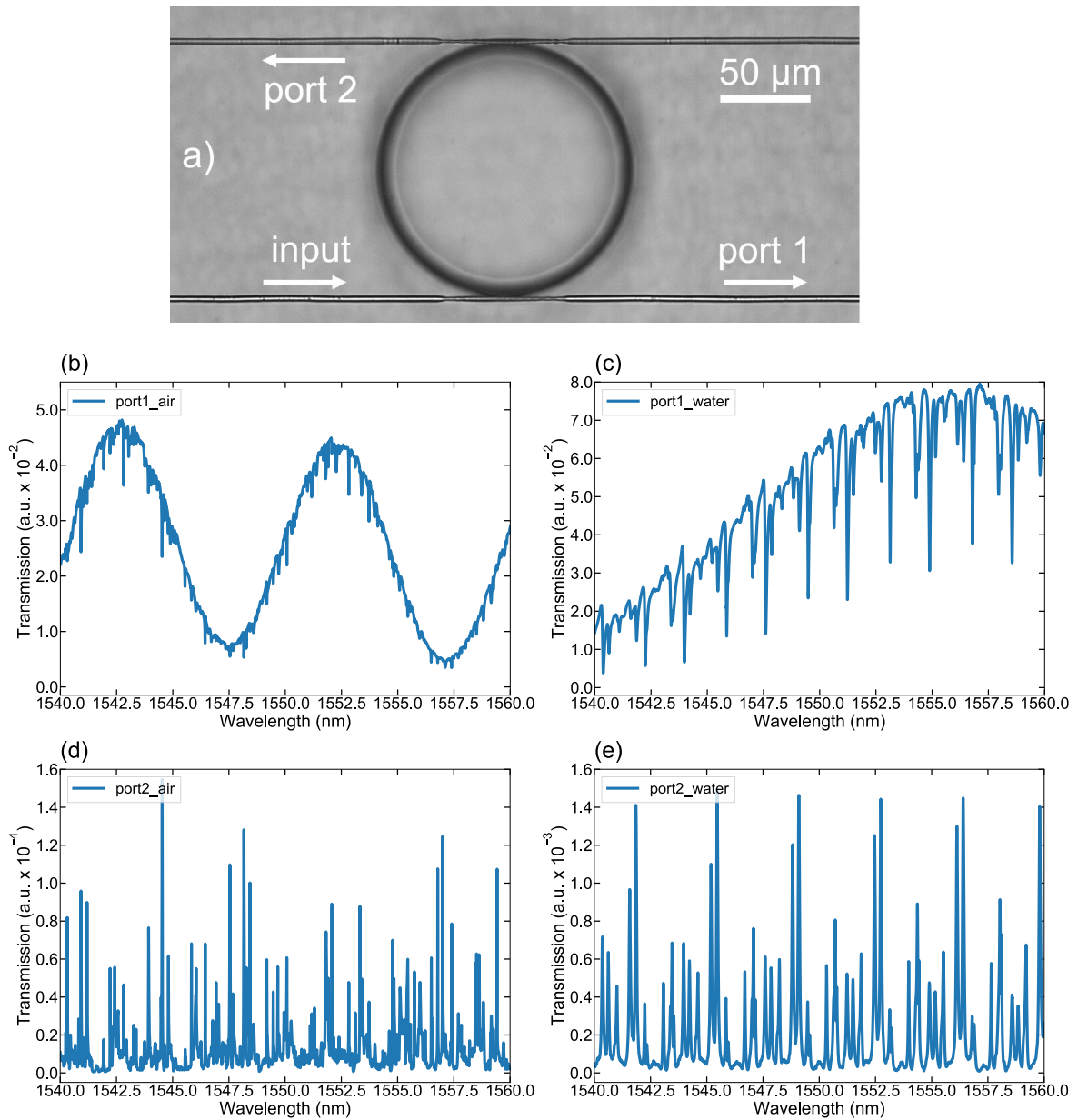


Figure 6.40: (a) Top view image of the two-port WGM resonator, and respective transmission spectra (b,c) at port 1 and (d,e) port 2 with air (left) and deionized water (right) surrounding the microstructures. The microdisk has a radius and height of 72 μm and 50 μm, respectively. The two suspended waveguides have different dimensions at their waist. To facilitate the analysis, all spectra are plotted in a linear scale.

6.5 Conclusions

This chapter focused on the construction of a label-free optofluidic sensor entirely made of fused silica, which integrates a whispering-gallery mode resonator excited by the evanescent field of a suspended waveguide inside a microfluidic channel. The device is fabricated by fs-laser micromachining followed by chemical etching and thermal annealing, which allows circumventing some issues usually observed when machining fused silica. The introduction of thermal annealing also decreases the surface roughness of both microstructures to tens of nanometres, thereby reducing scattering losses and improving the quality factor.

The fabrication of suspended waveguides is first studied. Solid-core liquid-cladding waveguide with core diameter as low as 3 μm were fabricated, comparable to the dimensions of tapered fibers. The guiding properties of the suspended waveguide were carefully analysed, having determined the fabrication parameters that minimize the coupling losses due to mechanical misalignment. Coupling losses as low as 0.4 dB/facet were obtained. Further, it was observed that the insertion loss profile of the suspended waveguide contains two periodical signals, on which arises from interference between the fundamental mode LP_{01} of the waveguide and light that travels unguided across the channel and another, observed when the waveguide is multimode, resultant from modal interference between the LP_{01} and LP_{02} modes. It was also demonstrated how the guiding characteristics of the waveguide and its loss profile can be reconfigured by changing the refractive index of the liquid surrounding it. In particular, this property may be of interest for photonic applications in optical switching or modulation, or in optical sensing as the studied analyte itself directly affects light propagation.

Coupling between the suspended waveguide and a microdisk resonator was then studied. In particular, the alterations made to the design and to the fabrication procedure, namely laser direct writing of the arc segment and thermally-induced morphing, can be used to overcome the limitations derived by the finite etching selectivity and, in turn, to accurately position the suspended waveguide tangent to the resonator. The versatility provided by fs-laser micromachining also enables accurate control of the dimension and geometry of both microstructures, in order to attain optimal phase-matching. Specifically, the control over the dimensions of the arc segment within the coupling region can be used to enhance the spatial overlap between the evanescent field of both modes and to improve optical coupling and increase the extinction ratio. The morphing tool described here solves numerous practical issues regarding the handling and the applicability of the device. The fabrication and experimental results are repeatable with no surface fouling being observed with the test fluids used on these experiments, while the monolithic construction guarantees that the suspended waveguide and resonator are robust and permanently aligned. Other results associated with surface fouling can, nonetheless, be observed with biological samples, but that was not assessed during this work. The device shows a sensitivity of 40 nm/RIU and a Q-factor around 2×10^5 for refractive indices near that of aqueous solutions. Although the sensitivity is of the same order of magnitude as the one reported for similar integrated and hybrid devices, the Q-factor is hundred times

greater [61, 67].

Still, some improvements can be made. The work should be complemented by numerical simulations in order to determine the appropriate dimensions and geometry of the suspended waveguide and microresonator that allow optimal phase-matching and operation at critical coupling. Additionally, improvements to the Q-factor can be made by increasing the annealing temperature or prolonging the duration of this process, in order to decrease the surface roughness and intrinsic scattering losses. Thermal treatment through CO₂ laser irradiation could also be tested as it significantly decreases the duration of this process into a matter of minutes, while it also confines the morphing only to the structures within the microfluidic channel. Further, a higher control between the distance of the suspended waveguide and the microresonator can be achieved by exploiting etchants with higher selectivity or etchants which attack the pristine material at a lower etch rate. This control is important to guarantee that the device operates in the critical coupling regime and to minimize extrinsic losses. Still, note that the measurement of the real gap can be possibly hindered by experimental issues, such as charge effects during SEM analysis. Flow-induced deflection of the suspended waveguide can also be considered as a post-fabrication mechanism to fine tune the coupling regime, with the added advantage of enabling this calibration for the surrounding medium under study [226]. In that context, it is also important to determine the limits of operation of the device by measuring the maximum flow rate supported by the microfluidic channel before causing breakage of the microstructures. A complete lab-on-a-chip device can also be formed by welding a cover glass, containing holes for fluid injection, to the silica substrate and by permanently gluing external optical fibers aligned to lead-in and lead-out waveguides. Albeit demonstrating its use as a refractive index sensor, the device can also be used for other applications. Given that the device is made entirely within a microfluidic channel, fluid handling capabilities can be easily incorporated. Further, the device is entirely made of fused silica, which is a primary material concerning biochemical compatibility. Accordingly, by functionalizing the surface of the microdisk, the device can be used for biosensing applications. Lastly, the work developed in this chapter takes special significance in the current state-of-the-art as it provides a means of fabricating silica-based structures with micrometric-size and in a user-defined architecture within a microfluidic channel.

Chapter 7

Conclusions and Future Work

The work presented in this thesis centred on the fabrication of optofluidic devices in planar fused silica substrates through fs-laser micromachining. Two possible configurations of such devices were demonstrated and their potential in optical sensing was proven. The design and the processing techniques used to produce these devices were discussed in detail. Special attention was devoted to the fabrication of microfluidic channels, while addressing some common issues observed when machining fused silica.

Although the focus is on the experimental applications enabled by this technology, an overview of the physical processes underlying fs-laser micromachining is essential to comprehend the laser-induced modifications observed, to optimize the fabrication process and to understand the limitations of this technique. This review is presented in chapter 2 where the modifications on fused silica resultant from laser exposure are highlighted. In particular, a tightly focused fs-laser beam ionizes the irradiated medium through non-linear absorption processes, which is followed by electronic relaxation and deposition of the laser energy within the lattice with consequent material modification.

Volume processing with high spatial resolution is made possible due to non-linear absorption, which confines the induced structural modification to a micrometric volume centred at the focus of the laser beam. Further, operation in a non-cumulative regime and the temporal dissociation between the excitation and relaxation processes prevents thermal effects and suppresses the formation of heat-affected zones, while also resulting in a replicable process. Moreover, movement of the substrate in relation to the laser beam focus enables the construction of pure 3D systems in unique architectures. In conjunction with the confined nature of the absorption process, this also enables spatially-targeted laser-induced modification which enables the integration of different classes of systems within a single planar substrate. All of these features linked to ultrafast laser inscription are difficult to come by when using conventional microfabrication processes, which is one of the reasons why this technology has been the subject of great interest in the realm of optofluidics. Depending on how much energy is deposited, two main modifications can be induced in fused silica: (i) isotropic increase of the refractive index due to densification, stress-accumulation or formation of defects which enables the construction of optical waveguides where light is guided along the modified path, and (ii) generation of etching selectivity due to the formation of nanogratings which facilitates the formation of

microfluidic channels by noting that the laser-modified volume is etched, in HF acid or in KOH solutions, at a higher rate than the surrounding pristine medium.

Still, the properties of both types of devices depend on the fabrication conditions due to the respective induced modification only occurring in a narrow processing window. This sets the need for an optimization of the fabrication process, which for optical waveguides can be found in the PhD thesis of Vítor A. Amorim and for microfluidic channels in chapter 4 of the present thesis. Microfluidic channels were designed by stacking multiple laser-exposure tracks periodically distributed along a 2-dimensional array. Perfect alignment of the nanogratings parallel to the axis of the microfluidic channel proved to be the defining factor to enhance the etching selectivity, which required the polarization of the fs-laser beam to be orthogonal to the scanning direction. Further, when writing at 500 kHz, the cross-section of the irradiated volume revealed two distinct modifications. The head of the laser-exposure track contained nanogratings which accelerate the etch rate, whereas its tail is formed by densified modified silica which lead to a weak etching selectivity. These observations indicated that HF acid should be used as etchant, as it translated into a much more uniform etched cross-section in comparison to what was obtained when using KOH. It was also found that the inscription conditions, namely pulse energy, translation velocity and separation between laser-exposure tracks, affected the etching dynamics. Higher pulse energies improved the etching selectivity, while also increasing the chances for fracturing due to relaxation of the accumulated stress. Spatial overlap of the multiple laser-exposure tracks reduced the surface roughness of the inner walls of the microfluidic channel, at the risk of cracking and while significantly increasing the exposure time as well. On the other hand, the duration of the irradiation and etching processes could be shortened by increasing the translation velocity. These observation resulted in a compromise between the inscription parameters, having determined the best conjugation of parameters to be: pulse energy of 60 nJ, scanning speed of 3000 $\mu\text{m/s}$, and horizontal and vertical spacing of 3 μm and 5 μm . These parameters ensured a high enough etch rate (longitudinal and vertical etch rates of 12 $\mu\text{m/min}$ and 2.7 $\mu\text{m/min}$, respectively) and led to crack-free microfluidic channels with smooth inner walls (sidewall and bottom surface RMS roughness of 20-30 nm and of 80-100 nm, respectively), minimal tapering (maximum angular deviation of 1°) and uniform aspect ratio, while minimizing the fabrication time. Based on this calibration, two examples of optofluidic devices were discussed in chapters 5 and 6.

In chapter 5, it was discussed the fabrication of a Fabry-Pérot interferometer composed by a microfluidic channel orthogonally intercepted by a fs-laser written waveguide, which is simultaneously used to excite and probe the etalon. The influence of the guiding characteristics of the optical waveguide on the spectral quality was assessed. Indeed, a low SNR was obtained when probing the Fabry-Pérot cavity with waveguides written at higher pulse energies due to the creation of defects associated with Mie scattering. Additionally, a low finesse was obtained when employing waveguides that exhibited higher insertion losses. Following these results, it was concluded that in order to improve the signal quality, the fs-laser written waveguides should be inscribed at

low pulse energies and low translation velocities. Besides being proven its application as a refractometer, the device was also used as a magnetic field sensor aided by the field-dependent refractive index property exhibited by ferrofluids that were injected inside the microfluidic channel. For this application, it was also verified that the surface chemistry resultant from the etching reaction with HF acid, led to an interaction with magnetic nanoparticles dispersed in the fluid which decreased the lifetime of the device. This issue had to be resolved by recurring to post-processing surface treatment. The results reported in this chapter again prove the need for a correct calibration of the fabrication parameters, in order to overcome some performance limitations not usually found in similar fiber-based devices.

A more ambitious application was demonstrated in chapter 6, where it was discussed the fabrication of microstructures inside a microfluidic channel through selective etching and assisted by thermal annealing. In particular, it was detailed the fabrication of a monolithic whispering-gallery mode resonator, consisting of a microdisk resonator coupled to a suspended waveguide responsible for exciting the optical modes of the resonator, with both structures being made inside a microfluidic channel for fluid handling capabilities. Thermal post-processing was performed due to two reasons, one of those being related to a reduction of the surface roughness and, in turn, to a decrease in the scattering losses and to an improvement of the intrinsic quality factor. At the same time, thermally-induced morphing shaped the microstructures into a minimum surface area configuration, which for the suspended waveguides led to an alteration from the initial rectangular cross-sectional profile to a circular one. In particular, straight solid-core liquid-cladding waveguides anchored to both walls of the microfluidic channel were realized with a minimum diameter of 2 μm over a 2 mm length, comparable to the typical size of tapered fibers. The guiding characteristics of these waveguides were studied both experimentally and numerically for different radii and against the refractive index of the cladding. Coupling losses lower than 1 dB were measured in the monomode regime, whereas the modes LP_{01} and LP_{02} were mainly excited in the multimode regime. Going back to the whispering-gallery mode resonator, optimization of the design and the realization of thermal annealing was also linked to the achievement of the desired geometry in the coupling region which enabled efficient excitation of whispering-gallery modes. Operation of the device as a refractive index sensor was demonstrated, having measured a Q-factor of 10^5 throughout the entire measurement range. In particular, these results encapsulate the potential of this technology for practical applications, where the monolithic construction ensures a robust and permanent alignment while solving issues connected to the handling and portability of the device.

A revision of the literature shows a fair share of articles discussing the fabrication of polymeric microstructures inside microfluidic channels. However, the use of polymers can compromise the performance of this device, especially when compared to its silica-based counterparts. Accordingly, the technique reported in chapter 6 expands the current state-of-the-art by providing a means for fabrication of silica-based microstructures with optical-grade quality inside a microfluidic channel. The fabrication of solid-core

liquid-cladding waveguides, or of more complex geometries such as microresonators or even of woodpile photonic crystals, where the fluidic medium defines the guiding characteristics, provides a direct interaction between light and fluid which can improve the sensitivity to variations in the surrounding environment. At the same time, the fabrication of microstructures amid the fluid flow can provide new processing capabilities of the microfluidic channel.

Improvements to the fabrication technique and to the devices reported in this thesis can still be made, as has also been disclosed in the respective chapters. A continuous study on the influence of the inscription and etching parameters is needed to further enhance the etching selectivity and to minimize the duration of the fabrication process, or to facilitate the design of other geometries, namely of microfluidic channels with curved surfaces. Adoption of other post-processing techniques, in particular of CO₂ laser annealing, would also improve the surface roughness while reducing to a question of minutes the duration of the annealing process. Throughout the thesis, the fabrication of pure lab-on-a-chips was also alluded to, but it was not examined in great detail. In particular, sealing of the microfluidic channel through bonding of a PDMS cover layer or laser welding of a glass cover to the surface of the fused silica substrate, and permanent binding of external optical fibers aligned to the fs-laser written waveguide through a photosensitive glue were swiftly considered. Although the proposed devices were successfully used for refractive index sensing, their optimal performance requires the design of the appropriate geometry and right dimensions of the device which can be determined through numerical simulations. Surface functionalization of the constructed microstructures also provides a more challenging, but also a more rewarding task of great interest in the domains of biosensing and analytical chemistry.

Lastly, the significance of this work is also linked to the work developed in the Centre for Applied Photonics of INESC TEC. Over the past five years, a lot of effort has been put into the study of micromachining processes assisted by ultrafast laser inscription with several publications having already resulted. In short, the work developed includes the inscription of optical waveguides in fused silica and in borosilicate glass planar substrates and the study of the guiding characteristics in both media; the inscription of waveguides at the surface of borosilicate glass and subsequent application in optical sensing through interaction with the fluidic medium surrounding the exposed waveguide; the fabrication of integrated optical devices, namely for power splitting or multiplexing, in fused silica; the fabrication of Bragg gratings and of long-period gratings in optical fibers and application in optical sensing; experimental studies on fluid flow through microfluidic channels and comparison with numerical results; the fabrication of polymeric microstructures through two-photon polymerization; and initial studies on fs-laser welding. In this sense, the results reported in this thesis expand the available arsenal of tools, from which more advanced devices can be envisioned.

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Appendix A

Cauchy and Sellmeier Parameters of Materials Used

Cauchy equation: $n = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4}$, λ in Angstroms

Medium	A	B	C
Cargille $n_D^{25^\circ C} = 1.3000 \pm 0.0002$	1.2955353	148840	2.155584e+11
Cargille $n_D^{25^\circ C} = 1.3100 \pm 0.0002$	1.3050713	166479	1.625594e+11
Cargille $n_D^{25^\circ C} = 1.3200 \pm 0.0002$	1.3146073	184118	1.095603e+11
Cargille $n_D^{25^\circ C} = 1.3300 \pm 0.0002$	1.3241434	201757	5.656121e+10
Cargille $n_D^{25^\circ C} = 1.3400 \pm 0.0002$	1.3336794	219396	3.562146e+9
Cargille $n_D^{25^\circ C} = 1.3500 \pm 0.0002$	1.3432154	237036	-4.943692e+10
Cargille $n_D^{25^\circ C} = 1.3600 \pm 0.0002$	1.3527514	254675	-1.02436e+11
Cargille $n_D^{25^\circ C} = 1.3700 \pm 0.0002$	1.3622874	272314	-1.554351e+11
Cargille $n_D^{25^\circ C} = 1.3800 \pm 0.0002$	1.3718235	289953	-2.084341e+11
Cargille $n_D^{25^\circ C} = 1.3900 \pm 0.0002$	1.3813595	307592	-2.614332e+11
Cargille $n_D^{25^\circ C} = 1.4000 \pm 0.0002$	1.3878691	434089	-4.450197e+11
Cargille $n_D^{25^\circ C} = 1.4080 \pm 0.0002$	1.3959156	429259	-3.333586e+11
Cargille $n_D^{25^\circ C} = 1.4160 \pm 0.0002$	1.4039621	424429	-2.216974e+11
Cargille $n_D^{25^\circ C} = 1.4200 \pm 0.0002$	1.4079854	422014	-1.658668e+11
Cargille $n_D^{25^\circ C} = 1.4240 \pm 0.0002$	1.4120086	419599	-1.100362e+11
Cargille $n_D^{25^\circ C} = 1.4320 \pm 0.0002$	1.4200551	414768	1.624995e+9
Cargille $n_D^{25^\circ C} = 1.4400 \pm 0.0002$	1.4281016	409938	1.132862e+11
Cargille $n_D^{25^\circ C} = 1.4480 \pm 0.0002$	1.4361481	405108	2.249474e+11
Cargille $n_D^{25^\circ C} = 1.4520 \pm 0.0002$	1.4401714	402693	2.807780e+11
Cargille $n_D^{25^\circ C} = 1.4560 \pm 0.0002$	1.4441946	400278	3.366085e+11

Table A.1: Cauchy coefficients for Cargille refractive index liquids series AA and AAA.

Sellmeier equation: $n = \sqrt{1 + \sum_i \frac{A_i \lambda^2}{\lambda^2 - B_i}}$, λ in micrometers

Medium	A_1	B_1	A_2	B_2	A_3	B_3
Air [227]	0.05792105	238.0185	0.00167917	57.362		
Fused Silica [228]	0.6961663	0.0684043	0.4079426	0.1162414	0.8974794	9.896161

Table A.2: Sellmeier coefficients of air and fused silica (Suprasil 1).

Appendix B

Suspended Waveguides formed through Self-Guiding Photopolymerization

This section discusses the possibility of fabricating suspended waveguides inside a microfluidic channel through self-guiding polymerization, as an alternative to the technique described in section 6.3. This method relies on light emerging from an optical waveguide (or optical fiber) to induce polymerization, spatially confined to the light propagation axis, of a photopolymer solution deposited at the end of the waveguide (fiber) [229, 230]. Although this technique has been successfully applied to the construction of micro-optical elements at the tip of an optical fiber [231] or to connect two single-mode or multimode fibers through a polymeric waveguide [232], it has yet to be applied in planar optofluidic devices.

The fabrication procedure starts by constructing, through fs-laser direct writing followed by chemical etching, the device shown in figure B.1 where two axially aligned fs-laser written waveguides orthogonally intercept a microfluidic channel. The laser direct writing process was conducted with the previous workstation held in place [119], in which a 0.55NA lens is used to focus the fs-laser beam. Accordingly, the irradiation parameters are slightly different than what has been used up until now. A microfluidic channel with cross-section of $100\text{ }\mu\text{m}\times 100\text{ }\mu\text{m}$ (width by height) was designed by stacking multiple laser-exposure tracks with constant spacing between each track of $3\text{ }\mu\text{m}$ and $5\text{ }\mu\text{m}$ in the horizontal and vertical plane, respectively. Each laser-exposure track was written along the axis of the microfluidic channel with a pulse energy of 100 nJ and translation velocity of $500\text{ }\mu\text{m/s}$, with the fs-laser beam polarized orthogonally to the perpendicular direction. The lead-in and lead-out waveguides were written $55\text{ }\mu\text{m}$ beneath the surface of the fused silica substrate, with a pulse energy of 400 nJ, translation velocity of $250\text{ }\mu\text{m/s}$ and with the fs-laser beam parallel to the scanning direction. Both waveguides end around $15\text{ }\mu\text{m}$ from the closest sidewall of the microfluidic channel. To avoid the “Quill” effect, the fs-laser beam scanned both waveguides along the same direction: the lead-in waveguide was written into the microfluidic channel and the lead-out waveguide was written outwards of the channel. Following laser direct writing, the substrate was etched in HF acid with a

10% volume concentration and in ultrasonic agitation for 60 minutes and, afterwards, the side facets of the substrate were mechanically polished to minimize the coupling losses to the lead-in and lead-out waveguides.

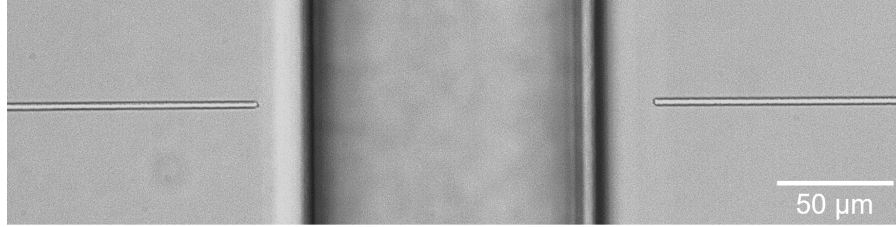


Figure B.1: Top view image of the device after fs-laser direct writing and chemical etching, and prior to photopolymerization. The lead-in waveguide (left) and lead-out waveguide (right) are aligned and orthogonally intercept the microfluidic channel.

Then, the microfluidic channel is filled with a free radical photopolymerizable liquid formulation provided by Dr. Olivier Soppera from the Institute de Science des Materiaux de Mulhouse (IS2M). This formulation contains a triacrylic monomer base PETIA, a xanthinic dye sensitizer Eosin Y in a 0.5% weight concentration, and a co-initiator MDEA in a 4% weight concentration. In addition, the monomer base also contains thermal inhibitors that provide stability to the formulation and impede thermally-induced photopolymerization. This formulation is photosensitive in a narrow wavelength range spanning from 450 nm to 550 nm, where incident light is linearly or non-linearly absorbed by the dye sensitizer (depending on the wavelength and peak intensity of the incident beam) which promotes the Eosin from the ground state to the singlet state, and then converts it from the singlet to the triplet state. Reaction between the Eosin in the triplet state and MDEA generates free radicals which react with the monomer base forming macroradicals in the initiation step which, after propagation and termination, are converted into a three-dimensional cross-linked polymer.

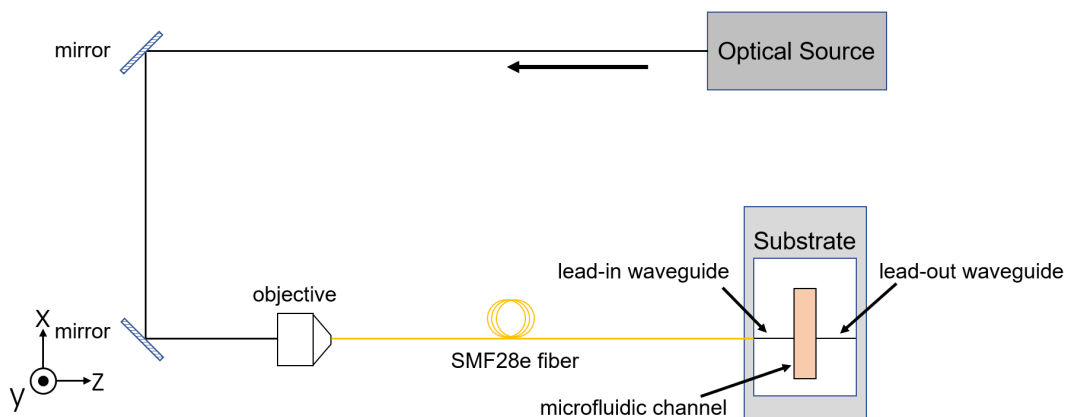


Figure B.2: Scheme of the optical setup used to photopolymerize the suspended waveguide inside a microfluidic channel made at the surface of a fused silica substrate.

According to the setup shown in figure B.2, light from a laser source is coupled into an SMF28e optical fiber via an objective lens (10× magnification and 0.25NA). Two mirrors

assembled on a parallel configuration and placed over a kinematic mount are used to optimize the optical coupling from the laser source to the fiber. The other end of the optical fiber is butt-coupled to the entrance of the lead-in waveguide, with index matching (Cargille series AA $n_D^{25^\circ\text{C}} = 1.4580 \pm 0.0002$) being used at the interface to minimize Fresnel losses. Light propagating through and emerging from the lead-in waveguide is launched into the microfluidic channel, where it is absorbed by the photosensitive formulation and induces a spatially-confined photopolymerization reaction; keep in mind that the polymerization is induced only from the lead-in waveguide. Due to competing effects, namely fluorescence of the liquid dye and oxygen quenching, which decrease the number of available free radicals capable of initiating polymerization, a threshold energy is required to polymerize the formulation. Accordingly, given that most of the optical power carried by the optical modes of the lead-in waveguide is confined to the core and due to the limited numerical aperture of the fs-laser written waveguide, the polymerization should occur predominantly along the light propagation axis where the incident intensity is highest. Further, as the reaction develops, the monomer solution (refractive index of 1.48 at 515 nm) is converted to a cross-linked polymer with higher refractive index (1.51 at 515 nm). The refractive index increase causes the light beam launched into the microfluidic channel to be mainly confined to the already polymerized volume, which counters diffraction and optical divergence and results in a self-guided process that gradually creates the suspended waveguide. The formation of the suspended waveguide is then similar to the physics behind the propagation of an optical soliton [233], resulting from the competition between diffraction of the incident beam and photopolymerization which tends to increase the refractive index where the light intensity is highest. The polymerization reaction is monitored *in situ* by observing through a microscope the fluorescence emitted from the Eosin, whose irradiated volume roughly coincides with the volume of polymerized material. The reaction is considered complete upon observation of bleaching, *i.e.* when no fluorescence is emitted, which means that all of the Eosin was consumed and, in turn, results in a stronger cross-linking degree. Afterwards, the microfluidic channel is rinsed in ethanol to remove the undeveloped polymer, leaving behind a suspended waveguide aligned with both fs-laser written waveguides and attached to both sidewalls of the microfluidic channel.

In comparison to the method described in section 6.3, self-guiding polymerization automatically guarantees that the suspended waveguide is aligned with both the lead-in and the lead-out waveguides. Moreover, photopolymerized microstructures display a lower surface roughness than its chemically-etched counterparts, which prevents the need for thermal annealing. At the same time, the writing of the lead-in and lead-out waveguides at the initial stages of the fabrication procedure (and together with the microfluidic channel) prevents some issues encountered when fabricating these structures after mechanical polishing, chemical etching and thermal annealing which translate in higher optical losses as was discussed in section 6.3.

In a first experiment, a MSL-FN-532 Single Longitudinal Mode Laser emitting a 532 nm continuous wave was used as radiation source. Figure B.3(a) shows a top view image of

the microfluidic channel after photopolymerization for 30 seconds with an incident laser power of 10 μW (measured at the output of the optical fiber). Although a suspended waveguide is formed connected to the lead-in and lead-out waveguides, several undesired features are observed: the waveguide is tapered and presents filaments visible closer to the right sidewall of the microfluidic channel, and the polymerization is also extended along the left sidewall of the microfluidic channel.

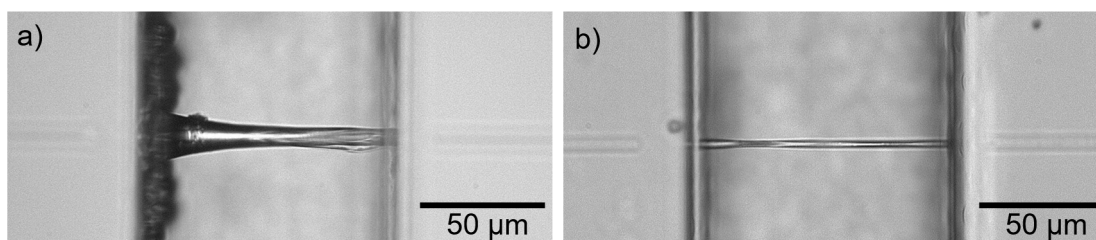


Figure B.3: Top view image of the microfluidic channel containing the suspended waveguide fabricated through (a) linear polymerization at 532 nm with an incident laser power of 10 μW for 30 seconds, and (b) 2PP at 1030 nm with an incident average laser power of 34 mW for 5 seconds. The laser power was measured at the output of the optical fiber. Light is incident from the left.

The tapered profile is attributed to the high concentration of the Eosin sensitizer which increases the absorbance of the formulation and favours polymerization at the entrance interface, while impeding the light beam from reaching the other end of the microfluidic channel until the Eosin at the entrance is fully consumed. A similar effect has been observed when fabricating microstructures at the tip of optical fibers, where a higher concentration of Eosin led to the formation of tapered tips while a lower concentration resulted in straighter tips [230]. On the other hand, filamentation can be due to the high incident power [234, 235] and/or due to interference between multiple optical modes propagating along the suspended waveguide as a result of its multimode nature at 532 nm [236]. Both effects (tapering and filamentation) could be solved by using a formulation with a lower concentration of Eosin, by reducing the incident power [233] and by performing a pre-polymerization step to reduce the refractive index contrast between the monomer base and the cross-linked polymer in order to support monomode propagation [237, 238]. However, neither of these solutions explains why photopolymerization also occurs along the sidewall of the microfluidic channel. Due to the high insertion losses of the lead-in waveguide at 532 nm (around 20-25 dB), light lost either in the fiber-to-waveguide coupling or due to scattering within the fs-laser written waveguide can continue to propagate unguided into the microfluidic channel and induce photopolymerization along the sidewall of the microfluidic channel. Therefore, the fs-laser written waveguide should be monomode and should exhibit low insertion losses at the actinic wavelength. A possible method to accomplish this is to subject the fs-laser written waveguides to thermal annealing at 900-1100°C for 2 hours [5]. Although this approach proved to better confine the polymerization reaction, it was observed that it still extended along the sidewall of the microfluidic channel.

To avoid these issues, the laser source was replaced by the fiber-amplified diode-pumped Amplitude Systèmes Satsuma HP laser emitting a 1030 nm train of 220 fs long pulses with a repetition rate of 500 kHz. With this source, the polymerization reaction is now based on two-photon absorption instead of linear absorption, which further restricts the polymerization to a narrower volume [239, 240]. Further, the insertion losses at 1030 nm are lower than at 532 nm (7 dB vs 20-25 dB). In addition, it is also possible to obtain simultaneously low insertion losses at 1030 nm (actinic wavelength) and 1550 nm (operating wavelength of the suspended waveguides), which was not achievable if the polymerization was to be performed at 532 nm. To obtain repeatable results and to minimize temporal broadening of the emitted fs-laser pulses, which reduce the peak intensity and increase the threshold energy for polymerization, a 50 cm long SMF28e fiber is used to couple light from the fs-laser to the lead-in waveguide.

Formation of suspended waveguides was only observed for incident powers higher than 16 mW (measured at the output of the optical fiber). Figure B.4 shows how the polymerization reaction develops for an incident power of 22 mW (also measured at the output of the optical fiber). At the initial stages of the reaction, the polymerization is confined to the entrance interface as denoted by the emitted fluorescence. By extending the reaction, the suspended waveguide gradually grows (from left to right) until it reaches the other end of the microfluidic channel after 2400 ms. The recorded frames also indicate that the polymerization is confined to the light propagation axis which implies a self-guiding process, as expected. Despite reaching the other end of the microfluidic channel, the reaction is prolonged past 2400 ms given that the formulation still emits fluorescence. In particular, the reaction should be stopped only after observing photobleaching, at which point a stronger cross-linking degree and a more rigid structure can be obtained. However, as shown in the time frame at 4800 ms, the suspended waveguide starts to bend downwards as the reaction is extended. Reasons for this feature are still unclear.

Figure B.3(b) shows a top view image of the suspended waveguide after irradiation at 34 mW (measured at the output of the optical fiber) for five seconds. By stopping the reaction after the suspended waveguide reaches the other end of the microfluidic channel and before observing any bending, it was possible to obtain a 3.5 μm wide straight waveguide aligned with both the lead-in and lead-out waveguides. Further, the surface of the suspended waveguide appears smooth and no rough edges are observed. Nevertheless, the waveguide is narrower at the entrance of the microfluidic channel which may be a result of self-focusing due to the high peak intensities of the incident fs-laser beam. In fact, if the incident average power at the output of the optical fiber is higher than 40 mW, the beam appears to collapse and multiple filaments are obtained instead.

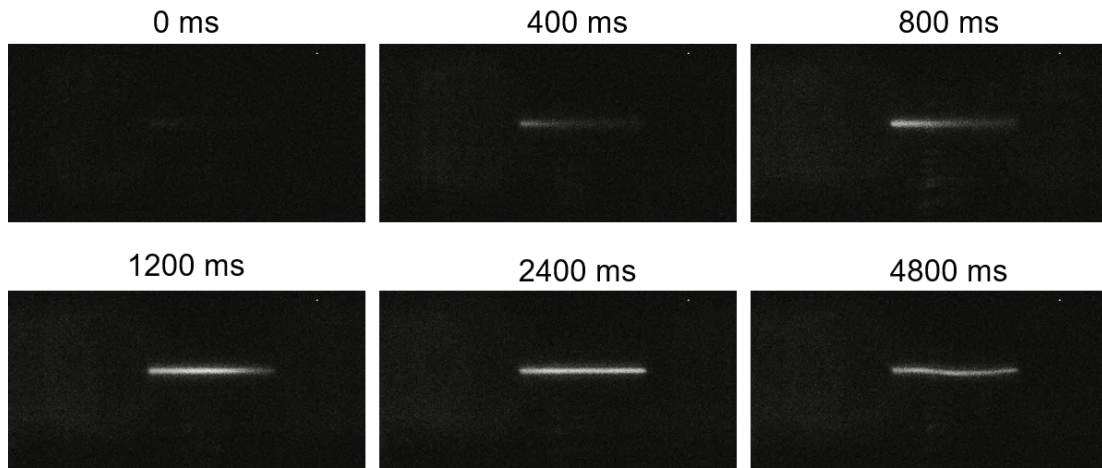


Figure B.4: Formation of the suspended waveguide at different time frames of the 2PP reaction. A 1030 nm laser beam with an average power of 22 mW (measured at the output of the optical fiber) is incident from the left. The build-up of the suspended waveguide is observed *in situ* due to the fluorescence emitted by the dye sensitizer.

It was concluded that straight tips could be obtained for incident powers between 16 mW and 40 mW and exposure times shorter than five seconds. Still, no light guidance was observed across the suspended waveguide. Further, the low exposure time means that the reaction is stopped before photobleaching, which results in an incomplete cross-linking that can lead to the formation of fragile tips that may be distorted or even broken when rinsing with ethanol, or to weak bounding to the sidewall of the microfluidic channel. To obtain a stronger bound to the interface, the polymerization can be done by irradiation from both fs-laser written waveguides [232], or by fabricating a Bragg grating waveguide within the lead-out waveguide which reflects the 1030 nm beam back into the suspended waveguide [240]. Although self-guiding polymerization can be used to form suspended waveguides inside microfluidic channels, the work presented throughout this section shows that the fabrication procedure and the irradiation parameters still have to be calibrated.