Fabrication methods and unit operations for multiphase direct fluorination in mini- and microreactors

Dissertation zur Erlangung des Doktorgrades der Technischen Fakultät der Albert-Ludwigs-Universität Freiburg im Breisgau

vorgelegt von

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Abstract

In this thesis, unit operations and fabrication methods were developed and analyzed to facilitate direct fluorination of liquid solvents in mini- and microreactors. The most challenging demands for these reactors were the harsh reaction conditions of direct fluorination which includes an excessive heat generation ($\Delta H = 470 \text{ kJ/mol}$) and highly corrosive reaction environment due to the aggressive reagents of fluorine and hydrogen fluoride (HF). Accordingly, for this purpose microfluidic components and fabrication methods were developed to enable this reaction in micro dimensions.

Micronozzles with a rectangular geometry were developed, which are able to generate monodisperse bubbles with a diameter of about 200 $\mu$m for the fluorine reaction into cross flowing liquid in a microchannel with a cross section of 300 $\mu$m $\times$ 300 $\mu$m. These nozzles were simulated and experimentally verified. Tests had shown that the generated bubble size can be varied by 8% with an aspect ratio variation of the nozzle opening. Furthermore, the impact of the nozzle orientation with respect to the liquid flow direction on the bubble size was evaluated. Nozzles with the narrow side in the liquid flow direction performed up to 3% smaller monodisperse microbubbles than an equivalent nozzle with the wide side in flow direction. Moreover, these experiments were extended to inverted and truncated pyramid-shaped nozzle channels realized with potassium hydroxide (KOH) etching and straight rectangular nozzle channels fabricated with deep reactive ion etching (DRIE).

A novel and simple microfabrication method was developed for electrochemical metal deposition inside a microfluidic structure. This patent pending process enables postforming of silicon based three dimensional microfluidic structures with a homogeneous and fluorine resistant nickel layer. An electroless plated 25 $\mu$m thick nickel layer was gas tight up to 6 bar and formed a fluorine inert protective layer for underlying silicon substrate of the microreactor. Moreover, this nickel layer sufficiently bonds different substrate layers of the microfluidic system which simplifies the microreactor fabrication process. Furthermore, subsequent selective KOH etching of the silicon substrate allows the release of these metal micropipes.

In this work, a minireactor system was established for pilot tests of the multiphase bubble flow, nickel passivation and bonding concept during the direct fluorination of ethylene carbonate (EC). The reactor ran with fluorine concentrations up to 88% over 100 h process time and no leakage nor corrosion of the nickel was detected. Temperature measurements showed a sufficient cooling of the highly exothermic reaction which occurred within a short time of 36 ms and, therewith, in a restricted hot spot area of the reactor. The reaction conditions in the continuous flow minireactor were stable and results in high reaction yields of 79% with a fluorine conversion of 95%.

For the use in the microreactor, the reaction microchannel for the multiphase reaction
was numerically optimized for mixing quality ($\alpha_V = 0.39$) and heat dissipation ($Nu = 13.6$). In combination with a micro heat sink, it was possible to dissipate 91% of the heat, emerging from the solvent in the reaction channel. In worst case scenario calculations, this microreactor system showed a sufficient heat dissipation with an acceptable maximum heat increase of 16 K at the hot spot.

The microfluidic units of bubble generation, reaction channel, active heat sink were integrated into a complete microreactor system and fabricated using the in-channel electroless nickel plating. Therewith, all requirements for successful direct fluorination in silicon based microreactors were solved. This enabled a realization of direct fluorination in the proceeding research work at this topic.

In addition to the microreactor design, the most promising microfluidic applications derived from the in-channel electroless plating process were analyzed in detail to confirm their advantages to comparable devices. This fabrication method facilitates three dimensional designed micropipes. The three dimensional structures showed a distinctive benefit of 150% to 170% better mixing quality of aqueous solutions at $Re < 200$ compared to equivalent two dimensional structures. Produced metal micropipes were partly released and thermal measurements showed their benefits compared to embedded microchannels. Three times higher heat flux densities and lower response times allow an accurate control of the temperature only with a variance of the surrounding cooling flow rate.
Kurzfassung

Im Rahmen dieser Doktorarbeit wurden Einheitsverfahren und Herstellungsmethoden für Mini- und Mikroreaktoren entwickelt und erforscht, um die Direktfluorierung von flüssigen Lösungsmitteln zu ermöglichen. Die größte Herausforderung für Reaktoren dieser Art waren die rauen Umgebungsbedingungen, die durch die Direktfluorierungsreaktion hervorgerufen werden. Dies beinhaltet eine exzessive Wärmeerzeugung (ΔH = 470 kJ/mol) und die enorm korrosive Reaktionsumgebung, die von den aggressiven Reaktanten Fluorgas und Fluorwasserstoff herrührt. Deshalb wurden in dieser Arbeit mikrofluidische Komponenten und Herstellungsmethoden entwickelt, die diese Reaktion in Mikrodimensionen ermöglichen.

Es wurden rechteckige Mikrodüsen entwickelt, die in der Lage sind, monodisperse Mikroblasen mit einem Durchmesser von 200 μm zu erzeugen. Die Blasen werden für die Direktfluorierung direkt in eine querfließende Flüssigkeit in einem Mikrokanal mit einem Querschnitt von 300 μm × 300 μm, eingeblasen. Diese Düsenformen wurden numerisch simuliert und experimentell verifiziert. Tests haben gezeigt, dass die erzeugte Blasengröße um 8% variiert werden kann, indem das Aspektverhältnis der Düsenöffnung verändert wurde. Zudem wurde der Einfluss der Orientierung der Düsenöffnung, in Bezug zu der Strömungsrichtung der Flüssigkeit, auf die resultierende Blasengröße untersucht. Düsen mit der schmalen Seite in Strömungsrichtung erzeugten 3% kleinere monodisperse Blasen als vergleichbare Düsen mit der breiten Seite in Strömungsrichtung. Diese Effekte wurde für zwei unterschiedlich hergestellte Düsen gezeigt. Die eine wurde mit Kaliumhydroxid (KOH) Ätzen hergestellt, was einer invertierten und abgeschnittenen pyramidenförmigen Düse entspricht, und die andere mit reaktiven Tiefenätzen (DRIE), welches gerade rechteckige Düsen erzeugt.


In dieser Arbeit wurde ein Minireaktorsystem für Anfangstests eingeführt. Diese Tests beinhalteten den mehrphasen Blasenfluss, die Nickelpassivierung und das
Verbindungskonzept während der Direktfluorierung von Ethylencarbonat (EC). Der Reaktor wurde über 100 h mit Fluorgas konzentrationen bis zu 88% gefahren und zeigte keinerlei undichte Stellen oder Korrosion. Temperaturmessungen zeigten das die hoch exotherme Reaktion effektiv gekühlt wurde und das die Reaktion innerhalb einer kurzen Zeit von 36 ms stattfanden. Dies bedeutet, dass die Reaktionswärme in einem sehr eingeschränkten Gebiet des Reaktors entsteht und auch gekühlt werden kann. Die Reaktionsbedingungen in dem Minireaktor mit kontinuierlichem Fluss waren stabil und resultierten in Reaktionsausbeuten von 79% und einer Fluorkonversion von 95%.

Für die Anwendung im Mikroreaktor wurde der Reaktionskanal numerisch für die Mischqualität ($\alpha_v = 0.39$) und Wärmeabfuhr ($Nu = 13.6$) optimiert. Zusammen mit einer aktiven Wärmesenke war es möglich, aus einer fließenden Flüssigkeit im Reaktionskanal 91% der Wärme abzuführen. Dieses Microreactor System zeigte bei einer überprüften worst case Szenario Rechnung eine effektive Kühlung mit einer annehmbaren maximalen Erwärmung von 16 K an dem größten Hitzebackpunkt.


Publications

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## Greek symbols

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<td>thermal diffusivity</td>
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<td>( \lambda )</td>
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### Abbreviations

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<td>CCD</td>
<td>charge-coupled device</td>
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<td>CFD</td>
<td>computational fluid dynamics</td>
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<td>DRIE</td>
<td>deep reactive ion etching</td>
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<td>EC</td>
<td>ethylene carbonate</td>
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<td>FFT</td>
<td>fast fourier transformation</td>
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<td>Fl</td>
<td>fluorescein</td>
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<td>KOH</td>
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<tr>
<td>LIGA</td>
<td>Lithographie, Galvaniformung, Abformung</td>
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<td>LPCVD</td>
<td>low pressure chemical vapor deposition</td>
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<td>MEMS</td>
<td>microelectromechanical system</td>
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<td>micro total analysis system</td>
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<td>piecewise linear interface construction</td>
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<td>poly(methyl methacrylate)</td>
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<td>PTFCE</td>
<td>polytrifluorochlorethylene</td>
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<td>reactive ion etching</td>
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<td>volume of fluids</td>
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<td>XPS</td>
<td>x-ray photoelectron spectroscopy</td>
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1 Introduction

In this chapter the motivation and aims of this work are given and structured in an outline. General informations of direct fluorination and a state of the art of microreactors for this chemical reaction are presented. Finally, the background for microfluidics, heat transfer, microfabrication and electrochemical deposition are briefly summarized.

1.1 Motivation & state of the art

Microreaction engineering comprises, in essence, a reactor with microstructured features (100 μm to 10 μm) for chemical reactions [1]. This new class of chemical microreactor systems has constantly emerged in the last decade, because the miniaturization provides unique process advantages for chemical reactions [1] and an outstanding, increased performance compared to commonly used batch reactors [2]. In the food, chemical, petrochemical and pharmaceutical industry, microreaction technology is considered as an innovative mean to improve the efficiency of chemical processes [1-3]. The benefits are mainly the improved selectivity and control of the chemical reactions [4-7], the large interfacial areas and the high heat and mass transfer rates due to small diffusion distances in micro dimensions.

One widespread working principle is the generation of a multiphase microchemical system by means of bubbles dispersed in a flowing liquid stream. Due to downscaling into micrometer dimensions, large reaction interface areas between the bubbles and the liquid substrate, as well as high heat and mass transfer rates are achievable [8]. The mixing time is shorter and heat is removed from the reaction much more efficiently than in conventional devices [8]. Moreover, microreactors can be integrated with active micro heat sinks and sensors for temperature and pressure monitoring during the reaction progress [9-14]. With these capabilities, microreactor systems enhance significantly the process control and heat management of harsh reaction conditions [4]. They are therefore able to perform highly exothermic reactions and new reaction pathways that are in most cases too difficult to handle in conventional equipment. Moreover, from an economical point of view this can be done with a minimal consumption of solvents, reagents and waste disposals costs due to the small dimensions and volumes [4-6, 15].

The small quantity of reagents involved will also, as an important aspect, greatly improve the safety of exothermic reactions. Microreactors prevent flow maldistributions and localized hot spots during a reaction which can lead, in worst case, to a runaway reaction [16, 17]. Even in the case of a microreactor failure, the small amount of chemicals could be easily contained [1].

At present, batch-wise chemical processing are standard practice in the industry.
Replacing batch with continuous flow reactors can notably decrease the process time [8, 18]. Furthermore, production throughput can be easily scaled-up with microreactors by increasing the number of several identical microreactors in parallel. This would eliminate a costly redesign from bench-top reactors to pilot plants and commercial scale production [18]. The up-scaling of miniaturized reactors also enables a distributed point-of-use production of chemicals with an acceptable investment into equipment. Pharmaceutical and fine chemical industries often require the manufacturing of small amounts of products and would benefit from approaches like that [1]. Concerning these potentials and advantages, microreaction engineering is increasingly used for different fields of chemistry. The progress of scientific and industrial research and already demonstrated applications show an ongoing development in the last decade. For more details about the development and applications of microreaction engineering please refer to the review articles of the group of Jensen [1, 3, 10] and the books of Ehrfeld et al. [8], Hessel et al. [19], and Kockmann et al. [2].

Our perspective for new reaction pathways with harsh reaction conditions in microreactors is the direct fluorination of organic solvents. The presence of fluorine imparts commercially attractive properties to these solvents like low surface tension, high thermal and chemical stability, and higher selectivity compared to the fluorine-free counterparts [20]. Fluorine-containing organic compounds play an important role in the fine and pharmaceutical chemistry [20]. Moreover, fluorinated compounds are used in various technical applications like fuel cells (e.g. direct methanol fuel cells), catalysis (e.g. fluorous phase reactions) and solvents for electrochemical energy storage devices (e.g. double layer capacitors, and lithium accumulators). In particular, the use of fluorinated compounds as liquid solvents in lithium ion accumulators shows growing interest due to the application in the increasing market for electric vehicle propulsion systems. The fluorinated compounds feature benefits like excellent oxidation durability, wide liquidus range and non-flammability that are interesting for safety issues in accumulators [21, 22].

However, their synthesis proves to be difficult: All indirect multistep fluorination techniques require expensive reagents, multiple process steps and have only a small overall yield [8, 17]. On the other hand, direct fluorination is not used today on a preparative scale due to difficulties in controlling the excessive heat generation of the reactions [20]. However, the direct fluorination of organic solvents in microreactors was already demonstrated by the groups of Chambers [7], Jähnisch [23], and de Mas [24]. These studies have shown the feasibility of running direct fluorination reactions in a microreactor and have demonstrated that the size reduction of the reactor features significantly improves the control of the reaction.

The work presented here was part of the research project “Direct fluorination in microreactors - WO 833/10-1” funded by the German Research Foundation (DFG). This project was a cooperation of the Laboratory of Molecular and Coordination Chemistry and the Laboratory for Design of Microsystems, both at the University of Freiburg. The target of the project was to conduct basic knowledge and first applications for direct
fluorine reactions of organic solvents in microreactors. Direct fluorination needs a precise control of the reaction conditions for an increased yield and a higher selectivity. These conditions are defined by the interfacial area between fluorine gas and the liquid substrate, the mixing quality and the temperature control with an integrated micro heat sink. Furthermore, the wetted surfaces of the reactor has to provide a long-term resistivity against the aggressive reactants fluorine and hydrogen fluoride. Therefore, the development of microfluidic unit operations for precise control of the reaction parameters and microfabrication methods for fluorine-resistive materials are the main aspects of the here presented work.

1.1.1 Direct fluorination

Elemental fluorine is under normal conditions a gas (F₂) and is one of the strongest oxidizing agents. It reacts with nearly every other materials at room temperature with a highly exothermic or even explosive reaction. Fluorine as part of organic molecules has a decisive effect on the physical and chemical properties. These effects are high thermal and chemical stability, low surface tension, and a low dielectric constant. Hence, organofluorine materials are an important class of chemicals. They are used in a broad field of applications like fluorinated polymers (teflon), liquid crystals (displays), solvents for electrochemical energy storage devices, uranium separation, and as intermediates for the synthesis of crop-saving agents and pharmaceuticals [25].

Organofluorine materials are commonly synthesized with complex indirect fluorinations where the heat of the reaction is distributed over several steps [20]. The three most common indirect methods are the oxidative fluorination, Halex, and Balz-Schiemann reactions with a main disadvantage of expensive reagents and a low yield [17]. The potentially efficient direct fluorination is feasible in microreactors at room temperature due to the effective heat dissipation.

In this work two different direct fluorination reactions were applied. These reactions provide the specifications for the microreactor with their physical properties and the emerging heat of the reaction. The direct fluorination of toluene (C₇H₈) appears as a benchmark to other microreactors and is displayed with a reaction scheme shown in Figure 1-1. It shows that one fluorine molecule binds to the toluene and the second reacts with the released hydrogen to hydrogen fluoride (HF). The reaction is highly exothermal with ΔH = 470 kJ/mol. It should also be mentioned that fluorine can react to three different fluortoluene isomers (ortho-, meta-, para-) due to the nature of the aromatic toluene.

The second reaction is the direct fluorination of ethylene carbonate i.e. EC (C₃H₄O₃) that is a promising reaction for further chemical research and for an application as solvent in lithium accumulators [26]. The fluorination of EC was chosen as model reaction, because of its symmetric simple molecular structure with just four hydrogen atoms. The reaction scheme of EC with fluorine is shown in Figure 1-2. The reaction heat is assumed
1.1 Motivation & state of the art

The reaction of EC with fluorine results in F₁EC [4-fluoro-1,3-dioxolan-2-one (A)] and hydrogen fluoride or F₂EC that occurs in three different isomers [cis-4,5-difluoro-1,3-dioxolan-2-one (B), trans-4,5-difluoro-1,3-dioxolan-2-one (C), and 4,4-difluoro-1,3-dioxolan-2-one (D)].

1.1.2 Microreactors for direct fluorination

Despite the advantages of microreaction engineering for the direct fluorination of liquid solvents, only few research groups are working on this topic worldwide. Three groups have reported their work of direct fluorination in microreactors but it is not known whether they have continued their research until today. These groups are Chambers et al. of the University of Durham, Jähnisch et al. with reactors of the Institute for Microtechnology Mainz (IMM) and de Mas et al. from the Massachusetts Institute of Technology (MIT). Chambers et al. and Jähnisch et al. demonstrated the feasibility of running a direct fluorination reaction with micromachined reactors in stainless steel and nickel. Chambers et al. [7, 15] used a single channel reactor, whereas, Jähnisch et al. [23] tested a micro bubble column with micro heat sink for the direct fluorinations. The group of de Mas et al. [9, 16, 24, 28] developed a sophisticated silicon based microreaction system with integrated micro heat sink and flow regime sensor. The used microreactors of these groups, a single channel reactor, a falling film reactor, a microbubble column reactor, and a microchip reactor are briefly described in the following. A review of these microreactors with a detailed overview of the functionality and
the performed chemical reactions is given by Löb et al. [29].

**Single channel reactor**

This device [7, 15] is a simple microreactor with a straight single channel (500 μm wide, 500 μm deep) cut into a nickel block and covered with a transparent polytrifluorochloroethylene (PTFCE) plate to seal the channel, see Figure 1-3. A capping made of stainless steal was placed on top of the PTFCE plate and the three parts were pressed together with screws. The 60 mm long fluidic microchannel is contacted with three borings providing a gas and liquid inlet and product outlet in the nickel block. Cooling channels are guided through the nickel block at the back side. The direct fluorination reactions of aromatics and dicarbonyls are carried out at total volume flow rate of 0.5 ml/h with a pipe flow regime at temperatures around 0 °C. The specifications of this reactor are given in Table 1-1.

**Microbubble column**

The microbubble column used in [23] comprises mainly a static micromixer to generate a total gas-liquid flow of 19 ml/h that is fed into a microchannel plate of 32 parallel microchannels (200 μm wide, 70 μm deep). These microchannels are 60.5 mm long and the reaction performs with a slug flow regime. An active mini heat exchanger cools the microreactor down to temperatures of -15 °C. The complete microbubble column is made of steel and electroformed nickel and schematically shown in Figure 1-4. All direct fluorinations of aromatics in this reactor are performed with maximum fluorine concentrations of 50%. Jähnisch et al. also used a second microreactor: This falling film microreactor is mainly a vertical nickel plate with microchannels to generate a liquid thin

![Figure 1-3: Schematic illustration of the single channel reactor of Chambers et al. [7].](image)
1.1 Motivation & state of the art

Film that is overflown with the fluorine-nitrogen gas mixture. The falling film microreactor showed a lower performance than the microbubble column and is therefore not described in detail here. The specifications of the microbubble column reactor are comprised in Table 1-2.

Table 1-1: Specification of the single channel reactor for direct fluorination.

<table>
<thead>
<tr>
<th>single channel reactor (Chambers)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>material</td>
<td>steel / nickel / PTFCE</td>
</tr>
<tr>
<td>fabrication</td>
<td>cutting</td>
</tr>
<tr>
<td>design</td>
<td>straight single channel</td>
</tr>
<tr>
<td>dimensions (width, depth, length)</td>
<td>500 μm, 500 μm, 60 mm</td>
</tr>
<tr>
<td>flow rate</td>
<td>0.5 ml/h</td>
</tr>
<tr>
<td>flow regime</td>
<td>pipe flow</td>
</tr>
<tr>
<td>reagents</td>
<td>aromatics, dicarbonyls</td>
</tr>
<tr>
<td>fluor concentration</td>
<td>&lt; 50%</td>
</tr>
<tr>
<td>reaction temperature</td>
<td>0 °C</td>
</tr>
</tbody>
</table>

Figure 1-4: Schematic illustration of the microbubble column reactor used by Jähnisch et al. [23].

Table 1-2: Specification of the microbubble column reactor for direct fluorination.

<table>
<thead>
<tr>
<th>microbubble column reactor (Jähnisch)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>material</td>
<td>steel / nickel</td>
</tr>
<tr>
<td>fabrication</td>
<td>etching / micromilling / electroforming</td>
</tr>
<tr>
<td>design</td>
<td>straight channel array</td>
</tr>
<tr>
<td>dimensions (width, depth, length; channel #)</td>
<td>200 μm, 70 μm, 60.5 mm; 32</td>
</tr>
<tr>
<td>flow rate</td>
<td>19 ml/h</td>
</tr>
<tr>
<td>flow regime</td>
<td>slug flow</td>
</tr>
<tr>
<td>reagents</td>
<td>aromatics</td>
</tr>
<tr>
<td>fluor concentration</td>
<td>&lt; 50%</td>
</tr>
<tr>
<td>reaction temperature</td>
<td>-15 °C</td>
</tr>
</tbody>
</table>
Microchip reactor

The group of de Mas et al. [9, 16, 24, 28] has developed a complete microreactor for direct fluorinations based on silicon microfabrication methods, see Figure 1-5. This is also the only research effort known until today using silicon MEMS technologies. The reactor comprises an active micro heat sink and a straight reaction microchannel array (20 channels, 20 mm long) with an integrated flow sensing device for every channel. All microchannels are fed by a liquid manifold. Gas is injected by nozzles into every channel (435 μm wide, 305 μm deep) and generates a multiphase flow of 4.5 ml/h. This flow is detected by the flow sensor to ensure the mainly used slug flow regime for the reactions. All channels were fabricated with potassium hydroxide (KOH) etching, covered with silicon oxide (SiO₂) and evaporated nickel and capped with a pyrex layer. The direct fluorination reactions of toluene were performed at 25 °C and with maximum fluorine concentrations of 25%. The specifications of the microchip reactor are comprised in Table 1-3.

Figure 1-5: (a) Schematic sketch and (b) a picture of the microreactor chip for direct fluorination of de Mas et al. [28]. (1) indicates the reaction channel array.

Table 1-3: Specification of the microchip reactor for direct fluorination.

<table>
<thead>
<tr>
<th>microchip reactor (de Mas)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>material</td>
<td>silicon / SiO₂ / nickel / pyrex</td>
</tr>
<tr>
<td>fabrication</td>
<td>silicon etching / nickel evaporation / anodic bonding</td>
</tr>
<tr>
<td>design</td>
<td>straight channel array</td>
</tr>
<tr>
<td>dimensions (width, depth, length; channel #)</td>
<td>435 μm, 305 μm, 20 mm; 20</td>
</tr>
<tr>
<td>flow rate</td>
<td>4.5 ml/h</td>
</tr>
<tr>
<td>flow regime</td>
<td>slug flow</td>
</tr>
<tr>
<td>reagents</td>
<td>aromatics (toluene)</td>
</tr>
<tr>
<td>fluor concentration</td>
<td>&lt; 25%</td>
</tr>
<tr>
<td>reaction temperature</td>
<td>25 °C</td>
</tr>
</tbody>
</table>
1.2 Goals of the thesis

The aim of this thesis is to facilitate the direct fluorination of liquid solvents in a silicon based microreactor system with an integrated micro heat sink. The reaction of fluorine gas with a liquid solvent proceeds mainly in the gas-liquid interface. Therefore, the control of the interfacial area is a decisive criterion and, if done properly a striking advantage for a precise reaction control. A generation of monodisperse microbubbles with adjustable size allows a control of the interfacial area and thus the reaction rate. The microchannel design enables an optimal mixing of the reactants and an effective heat conduction out of the liquid. The heat conducted out of the microchannel, is absorbed by an active microstructured heat sink. Microfabrication technology allows for a precise control of the reactor features in microdimensions. Moreover, microfabrication in silicon facilitates, in principle, a large scale fabrication of the microreactor. However, the silicon substrate exhibits problems concerning the handling of the highly aggressive reagents fluorine and hydrogen fluorine. Due to this fact, silicon has to be covered with a chemically resistant metal layer to withstand the highly corrosive direct fluorination environment. This metal layer has to encapsule the reactor gas-tight and bond the individual reactor layers together. This divides the work into the following tasks:

- microbubble generation,
- corrosion resistant metal coating of structured silicon substrates,
- fabrication method for gas-tight metal microchannels and micronozzles,
- effective heat dissipation in the microreactor,
- proof of concept with a minireactor, and, finally
- implementation into a microreactor system.
1.3 Thesis outline

This thesis comprises the developments of microfluidic unit operations and new fabrication methods for a microfabricated multiphase reactor for direct fluorinations. According to the goals of this work, the following is covered:

- introduction into the topic of direct fluorination, microreaction engineering and a theoretical background for microreaction engineering (this chapter 1).
- theoretical approach, numerical simulations and experiments on monodisperse microbubble generation with a geometric variation of rectangular micronozzles for the specific application in a direct fluorination microreactor (chapter 2).
- material research of different electrochemically deposited metals and development of an in-channel electroless plating process to fabricate gas-tight and chemically inert metal micropipes (chapter 3).
- design, fabrication and first direct fluorination reactions in a minireactor system as a proof of concept for multiphase flow, nickel passivation, and bonding technologies intended for the microreactor (chapter 4).
- implementation and functionality tests of all unit operations (bubble generation, micromixing, heat dissipation) and fabrication methods (electroplating, in-channel electroless plating) into a complete microreactor system (chapter 5).
- investigation of a three dimensional microchannel mixer and a freestanding micropipe heat sink as further applications for the in-channel electroless plating process (chapter 6).
- a conclusion and an outlook of the thesis (chapter 7).

The work of the chapters 1, 2, and 3 have already been published or has been prepared for submission to scientific conferences or journals. The respective references are explicitly listed in the preface of this thesis.
1.4 Theoretical background

1.4.1 Principles of microfluidics

Microreaction engineering benefits primarily from the effects of miniaturization of the fluidic components. The surface area to volume ratio increases with decreasing linear dimensions. According to this, physical properties of the surfaces start to dominate and the fluid flow in micro dimensions is expected to be laminar. Furthermore, surface tension plays an important role and increases the effect of capillary forces. These characteristics can be categorized by dimensionless parameters that are valid independent of the exact scale of the system. This section gives a brief discussion about fluidic properties and the dimensionless parameters in micro dimensions. For more details please refer to microfluidic handbooks, e.g. of Bruus [30], Tabeling [31], Gad-el-Hak [32], or Nguyen [33].

The information about the flow regime is given by the dimensionless Reynolds number $Re$ that expresses the ratio of inertial forces to viscous forces. In channels it is defined as

$$Re = \frac{\bar{v} \cdot d_H}{\nu}, \quad (1.1)$$

with the mean velocity flow $\bar{v}$ and the kinematic viscosity $\nu$ [33]. The characteristic length scale is the hydraulic diameter $d_H$ of the channel. For a square channel it is determined to

$$d_H = \frac{2 \cdot w \cdot h}{(w + b)} \quad (1.2)$$

where $w$ is the width and $b$ the height of the channel [32]. The Reynolds number allows to compare fluid flows of different liquids and in different channel dimensions. A change from laminar to turbulent flow is usually assumed when the inertial forces are multiple times higher than the viscous forces. The minimum requirements for a turbulent flow are normally considered to be present above the critical Reynolds number of $Re_{crit} = 2300$. Commonly, the Reynolds numbers of microfluidic systems are much lower due to the small dimensions. Hence, the flow characteristics of microfluidic systems are usually strictly laminar.

Along a microfluidic channel with laminar flow, the pressure loss is an important factor that represents the effort to be taken to generate a certain flow rate. The pressure loss over a long microchannel length $l$ is calculated by [32]:

$$\Delta p = \zeta \cdot \frac{l}{d_H} \cdot \rho \cdot \frac{\bar{v}^2}{2}. \quad (1.3)$$
When the liquid flows in a quadratic channel, the Fanning friction factor $\xi$ is given by [32]:

$$\xi = \frac{14.3}{Re}. \quad (1.4)$$

For a hydrodynamic description of microfluidics, it is assumed that the fluids are Newtonian fluids. This means that the viscosity of the fluids, gases and simple liquids, are constant with dimensional scaling. The used fluids are also expected to be incompressible, which means that their density $\rho$ is constant. This is reasonable, when the velocity $v$ of the fluid is much less than the speed of sound $v_s$ in the fluid. The resulting dimensionless number is the Mach number:

$$Ma = \frac{v}{v_s}. \quad (1.5)$$

Fluid flows with $Ma < 0.3$ can be assumed as incompressible [32]. In the case of multiphase flow the interfacial forces increase with miniaturization. This is represented by the Weber Number

$$We = \frac{\rho \cdot v^2 \cdot d_H}{\sigma}, \quad (1.6)$$

that relates the inertial forces and the surface forces with the surface tension $\sigma$ of the fluid over the characteristic length scale $d_H$. The relation of gravitational force and surface force is described by the Bond number

$$Bo = \frac{\Delta \rho \cdot d_H \cdot g}{\sigma}, \quad (1.7)$$

where $g$ represents the constant of gravitation. For multiphase flow the density is replaced by the density difference of the two fluids $\Delta \rho$. With exceptionally small Weber and Bond numbers of $We \ll 1$ and $Bo \ll 1$, the gravitational and buoyancy forces can be neglected because surface forces dominate gravitational and inertial forces.

For immiscible shear flows the relation of the viscous force and the surface tension is represented by the Capillary number

$$Ca = \frac{\rho \cdot v \cdot \nu}{\sigma} = \frac{We}{Re} \quad (1.8)$$

which can also be expressed by the Weber and Reynolds number. The capillary number is used to indicate the bubble or droplet break-up and the deformation in an immiscible liquid flow.
1.4 Theoretical background

1.4.2 Heat transfer in microchannels

The miniaturization of the fluidic components increases the heat and mass transfer due to the increased surface area to volume ratio. This is an important benefit of microreactors that enables temperature control of highly exothermic reactions. For heat conduction problems with surface convection effects the impact of the miniaturization is interpreted with the Biot number

$$Bi = \frac{\alpha \cdot V_s}{\lambda_s \cdot A_s} = \frac{R_{\text{cond}}}{R_{\text{conv}}}$$  \hspace{1cm} (1.9)

which provides a relation of the temperature difference in the solid relative to the temperature drop between the surface and the fluid. The Biot number is described by the thermal diffusivity $\alpha$ that describes heat flux at the wall with the area $A_s$ and the heat conductivity of the solid $\lambda_s$ with the volume $V_s$. For $Bi < 0.1$ the conductive resistance $R_{\text{cond}}$ is much smaller than the convective resistance $R_{\text{conv}}$. Hence, the convective heat transition has a much bigger impact than the conductive heat transition and it is reasonable to assume an uniform temperature distribution over the solid volume. This fact is significant for transient heat conduction problems.

Thermal resistors are analog to electric resistances and, therefore, treated in an analogon to Ohm’s law. In this application, two types of thermal resistors exist, the conduction and the convection resistances. Within a material, the conductive resistance

$$R_{\text{cond}} = \frac{l}{\lambda_s \cdot A_s}$$  \hspace{1cm} (1.10)

is across the length $l$ of the material with the thermal conductivity $\lambda_s$ and the cross sectional area $A_s$ of the conducting heat path in the material. The convective resistance

$$R_{\text{conv}} = \frac{1}{\alpha \cdot A_s}$$  \hspace{1cm} (1.11)

describes the heat transfer by convection at a surface area $A_s$ with the thermal diffusivity $\alpha$. This heat transfer coefficient depends for fluids on the Nusselt number ($Nu$) and, as a consequence, on the Reynolds number ($Re$). Again, the dimensions of the fluidic reference system are defined by the hydraulic diameter ($d_{\text{H}}$).

The phenomenon of convective heat transfer out of the fluid into the channel wall is described by the dimensionless Nusselt number

$$Nu = \frac{\alpha \cdot d_{\text{H}}}{\lambda_f}$$  \hspace{1cm} (1.12)

with the heat conductivity of the fluid $\lambda_f$ and the hydraulic diameter of the microchannel $d_{\text{H}}$. The Nusselt number is constant for laminar flow at low Reynolds
numbers, \( \text{Re} < 10 \). With increasing volume flow the Reynolds number increases the Nusselt number due to vortices generated at the channel entrance and at channel bends. The calculation of the Nusselt number for microfluidic channels is an intensively discussed topic for micro heat sinks and still not solved in general [34-36]. The classical approach for a mean Nusselt number [37] is

\[
Nu = 0.664 \cdot \sqrt[3]{Re \cdot Pr},
\]

with the Reynolds number and the Prandtl number

\[
Pr = \frac{c_l \cdot \eta}{\lambda_1} = \frac{\nu}{\alpha},
\]

which is a measure of the relative influences of thermal conductivity \( \lambda_1 \), heat capacity \( c_l \), and dynamic viscosity \( \eta \) of the liquid. It is also the ratio of the momentum diffusity i.e. kinematic viscosity \( \nu \) to the thermal diffusivity \( \alpha \).

### 1.4.3 Microfabrication

As comprehensive literature is available on this topic, only a brief summary of the microfabrication processes used in this thesis is given here. For further information please refer to handbooks for microfabrication [32, 38-41]. In cases where a more detailed description of the processes is needed, they are presented in the respective chapter.

The patterning of the microfluidic structures in \(<100>\) silicon (Si) wafers was done with standard photolithography. These pattern were transferred into silicon oxide (SiO\(_2\)) or silicon oxide + silicon nitride (SiO\(_2\) + Si\(_3\)Ni\(_4\)) layers with reactive ion etching (RIE). All Si\(_3\)Ni\(_4\) layers were deposited by low pressure chemical vapor deposition (LPCVD). The SiO\(_2\) layers were thermally grown on Si or deposited by plasma enhanced vapor deposition (PECVD). The microfluidic structures were etched into the silicon bulk with deep reactive ion etching (DRIE) or potassium hydroxide (KOH) etching. DRIE was used for deep trenches in the bulk and KOH was preferred for structures with slanted walls. The structured silicon wafers were covered with a palladium layer by vapor-deposition. This layer is the starting layer for the subsequent electrochemical metal deposition.

### 1.4.4 Electrochemical deposition

Besides the microfabrication technologies electrochemical deposition is a process to create electronic components, surface coatings, and three-dimensional electroforming for MEMS applications. The process of electrochemical deposition is basically the reduction of metal ions from aqueous electrolytes. In general, two processes can be used to provide the electrons for the reduction reaction. Electroplating provides the electrons via an external power supply, whereas electroless plating provides the electrons with reducing agents added to the electrolyte.
1.4 Theoretical background

Electroplating is well established for microelectronic and MEMS application. This fabrication method is well described in its general properties by several publications, e.g. Schlesinger [42] and Kanani [43]. For MEMS applications please refer to Ghodssi and Lin [41] and Pauleau et al. [44]. The process of electroless plating was used in this thesis as a new deposition method inside a closed microfluidic channel and is therefore explained in more detail in the following.

**Electroless plating**

Electrochemical plating involves oxidation and reduction reactions with an electron transfer between the reacting chemical species. This is shown in the reaction equation [46]:

\[
\text{Red}^{n+} \rightarrow \text{Red}^{(n+z)+} + z \cdot e^{-} \\
\text{Me}^{z+} + z \cdot e^{-} \rightarrow \text{Me}^{0}.
\]  

(1.15)

Electroless plating needs no external current source because the electrons for the reactions are provided by the reducing agents (Red) that reduce the metal ion (Me\(^{z+}\)) to a metal atom (Me\(^0\)). This happens with an oxidation of the reducing agent at the same time. Complexing agents prevent an uncontrollable reaction in the electrolyte solution and not at the substrate surface. With these complexing agents, the substrate surface has to act as a catalyst to initiate the reaction. The surface adsorb the electrons of the reducing agent and transfers them to the metal ions which reduce to a metal atom, bonded to the surface. This is schematically shown in Figure 1-6. Additionally to the metal deposition, also the reduction agents partly deposit on the catalytic surface. Hence, the electroless plated metal layer is an alloy of metal and reduction agent. Besides the salt for the metal ions, the reduction agent, and the complexing agents the electrolyte solutions consists of other components. Bases and acids define the pH-value that is stabilized by buffer solutions.

![Schematic model of electroless plating with the catalytic electron transfer from the reducing agent (Red\(^{n+}\)) to the metal ion (Me\(^{z+}\)) that is reduced to a deposited metal atom (Me\(^0\)) on the substrate surface.](image)

Figure 1-6: Schematic model of electroless plating with the catalytic electron transfer from the reducing agent (Red\(^{n+}\)) to the metal ion (Me\(^{z+}\)) that is reduced to a deposited metal atom (Me\(^0\)) on the substrate surface.
In this thesis electroless nickel is used for the metal plating. The reaction of the chemical deposition can be written as follows:

\[
\text{NiSO}_4 + \text{NaH}_2\text{PO}_2 + x\text{H}_2\text{O} \rightarrow \text{Ni}^0 + \text{NaH}_2\text{PO}_3 + 2\text{H}_{\text{ads}} + 2\text{H}^+ + \text{SO}_4^{2-}, \quad (1.16)
\]

and

\[
2\text{NaH}_2\text{PO}_2 + 2\text{H}_{\text{ads}} \rightarrow \text{NaH}_2\text{PO}_3 + \text{P} + \text{NaOH} + x\text{H}_2\text{O}. \quad (1.17)
\]

The first reaction in Eq (1.16) describes the nickel deposition on the catalytic substrate. The nickel is part of nickel sulfate (NiSO\(_4\)) and is reduced to nickel (Ni) with the reduction agent sodium hypophosphite (NaH\(_2\)PO\(_2\)) due to the catalytic electron transfer. From this reaction results also hydrogen as ions (H\(^+\)) or adsorbed at the surface (H\(_{\text{ads}}\)) and sulfations (SO\(_4^{2-}\)). The deposited nickel directly interacts with sodium hypophosphite to give way for a phosphorous codeposition. Therefore, the deposited metal layer is an alloy of nickel and phosphorous with, however, a very low phosphorous concentration. This is shown in the side reaction Eq (1.17). Here, the deposited phosphorous (P) is generated from sodium hypophosphite, together with orthophosphite (NaH\(_2\)PO\(_3\)), sodium hydroxide (NaOH) and water (H\(_2\)O). During the electroless plating more sulphuric acid is generated than sodium hydroxide, because more nickel is deposited than phosphorous. Hence, the pH-value in the electrolyte solution decreases during the plating process. As the electroless nickel process depends on the pH-range, a variation of the pH-value can change the deposited layer quality or even stop the plating process.

The books of Riedel [45] and Mallory [46] give a detailed summary of electroless plating in general. For electroless plating in MEMS applications Ghodssi and Lin [41] and Pauleau et al. [44] show an overview and relevant plating procedures. Furthermore, the work of Furukuwa et al. [47, 48] shows electroless nickel plating for high aspect ratio microstructures.

The biggest benefits of electroless plating are the deposition without an external current source, the homogeneous layer thickness, a selective deposition, and the possibility of metallization inside a substrate. These benefits are crucial for microstructures. Especially for microfluidic structures with high aspect ratios and sharp edges a homogenous layer deposition is favorable. Furthermore, the metallization by electroless plating inside a substrate opens completely new possibilities for microfluidic and MEMS technologies.
1.5 References


2 Bubble generation

2.1 Introduction

For multiphase microreactors an understanding of the bubble generation, their dimension and exact shape is essential. Significant efforts have been devoted to the understanding of bubble generation [1]. Physical models for bubble generation in static cases [2] and with cross flowing liquid [3] were developed, but they are still diversely discussed and continuously improved [1–5]. In general, the generation of small size bubbles is recognized as a process of major difficulty [6]. Here, microfluidics offers a promising new route to generate highly uniform bubbles in the 10 μm - 100 μm size range. Due to their identical size, these monodisperse microbubbles enable constant chemical reaction conditions. In addition, this reduces the risk of Ostwald ripening due to the reduced Laplace pressure difference of the bubbles [7]. Numerous authors have demonstrated the ability to make highly monodisperse microbubbles by transporting two immiscible fluids in a microchannel [8–15]. Several approaches to generate monodisperse microbubbles in such a co flowing liquid were discussed in literature by using T-junctions [11], microbubble columns [14], or capillary flow-focusing devices [8, 13]. However, the T-junction and the microbubble column restrict the minimum size of monodisperse bubbles to the dimensions of the fluid channel and generate a slug flow instead of bubbly flow. This is not desirable for many chemical reactions since the slug flow provides an additional, undesired gas-solid interface. Finally, the capillary flow focusing technique is very sensitive to changes in the volume flows which generates different bubble sizes.

The here presented research aims on the design and the realization of a new multiphase microreactor concept for a direct fluorination of aromatic molecules. The fluorination is run by direct injection of fluorine gas bubbles with a radius of about 100 μm into a liquid organic solvent. Since fluorine has a low solubility in commonly used organic solvents, the reaction proceeds at the gas-liquid interface, which therefore determines the fluorination process [16]. This implies that the large interface, besides the much better temperature control, allows to handle the delicate direct fluorination process. A flexible generation of microbubbles at high frequencies allows to regulate the effective interface area for the chemical reaction and thus the reaction rate. To reduce the influence of the fluid flow and medium characteristics during monodisperse microbubble generation a novel concept of bubble formation via rectangular nozzles is used. In detail, nozzle designs with different aspect ratios with respect to rectangular nozzles are investigated, and presented [17–19].

The following chapter focuses in the first part on the theoretical analysis for the dominating physical behavior of microbubble generation at rectangular nozzles. A
simplified analytical model is developed to identify the major influencing parameters. The main focus of this work is the influence of the nozzle shape on the generated bubble size. In more detail, the nozzle shape and the other parameters affecting the microbubble formation are investigated with computational fluidic dynamics (CFD). The second part of the chapter describes the design, fabrication and characterization of different rectangular micro nozzles for the generation of the monodisperse microbubbles in a cross flowing liquid. Silicon and pyrex are used as structural materials for the main microchannels. The nozzles were realized in one side wall of the main microchannels with deep reactive ion etching (DRIE) or potassium hydroxide (KOH) etching, to obtain different shapes of the nozzle channels. The microbubbles injected with different nozzle geometries into the main channel were analyzed with a high speed camera and a photosensitive measurement setup to show the effect of the nozzle shape on the generated bubble size.

2.2 Theory

To understand the main principle of bubble generation in a microfluidic regime this section starts with introducing a simplified analytical model. It provides already a clear indication of the influence of fluid rheology, velocities and the nozzle geometry on the resulting bubble dimensions. The outlined model merges different basic approaches from different disciplines of fluid mechanics to describe bubble generation in a microfluidic system. Primarily, this model point out the influence of the nozzle geometry on the resulting bubbles.

In the microreactor the bubble is generated in a cross flowing liquid. The disperse gas phase enters through a single rectangular nozzle in the sidewall of a microchannel with a quadratic cross section. An individual gas bubble starts to grow at the nozzle orifice, then further expands into the cross flowing liquid with a connecting hose to the gas volume in the nozzle channel, until it reaches a critical size and then completely detaches from the orifice. In this critical snap-off moment, the detaching forces acting on the bubble overcome the retaining forces induced by the connecting hose. A schematic drawing of this critical state is shown in Figure 2-1. The gas bubble is generated by a constant gas volume flow, $V_g$. We consider a constantly flowing liquid, with its volume flow $V_l$ not being disturbed by the emerging spherical gas bubble. The fluids are assumed to be isothermal and incompressible. As the size of the bubbles is in the micro scale, the gravitational and buoyancy force can be neglected. This is characteristic for microfluidic systems where surface forces dominate gravitational and inertial forces. These micro scale phenomena are reflected in small Bond and Weber numbers for this system ($Bo << 1$, $We << 1$), see subchapter 1.4.1.

The bubble is retained by the force $F_{sp}$, generated by the static pressure differences. $F_{sp}$ represents the dynamic effect of the pressure difference between the gas and liquid phase of the growing bubble. In addition, the force of the gas phase adhesion, $F_\sigma$ at the smallest restriction of the bubble neck retains the gas bubble at the orifice. These two forces were
proposed by Schröder et al. [20] for emulsification and are given by:

\[ F_\sigma = U_n \cdot \sigma \quad \text{and,} \]

\[ F_{sp} = (p_g - p_l) \cdot A_n = \frac{4 \sigma}{d_b} \cdot A_n, \quad (2.2) \]

where the cross sectional area \( A_n \) and the circumference \( U_n \) are taken at the narrow restriction of the bubble neck and \( d_b \) is the diameter of the spherical bubble. The interfacial tension, \( \sigma \) is influenced by the size of the growing bubble and is neither constant nor uniform when the bubbles are disrupted. To simplify this complex behavior, it is assumed that \( \sigma \) takes the value of the balance interfacial tension between the two fluids in the moment of snap-off.

The main detaching force is the viscous drag force, \( F_d \) due to the liquid phase flowing past the droplet, parallel to the nozzle opening. We expect that the flow behavior during the bubble grow is similar to the flow around a spherical body. With this assumption the viscous drag force can be defined as

\[ F_d = c_d \cdot \frac{\rho_l \cdot v_l^2}{2} \cdot \frac{\pi \cdot d_b^2}{4} \quad (2.3) \]

where \( \rho_l \) is the density and \( v_l \) the mean velocity of the liquid. The drag coefficient \( c_d \) can be assumed for laminar flow with [21]
and the Reynolds number $Re$ for the liquid flow in the quadratic channel is given by

$$Re = \frac{\nu_l \cdot d_H \cdot \rho_l}{\eta_l}$$  \hspace{1cm} (2.5)$$

where $d_H$ is the hydraulic diameter and $\eta_l$ the dynamic viscosity of the liquid. To calculate the Reynolds number with the hydraulic diameter is a simplification to calculate the drag coefficient $c_d$, because we assume, that the final bubble takes approximately two-thirds of the fluid channel’s hydraulic diameter. The asymmetric flow profile in the partly obstructed liquid channel generates the dynamic lift force $F_{dl}$ which is directed to the core flow of the liquid [22] and represents a detaching force:

$$F_{dl} = 0.761 \cdot \frac{\tau_w^{1.5} \cdot d_b^3 \cdot \rho_l}{\eta_l}$$  \hspace{1cm} (2.6)$$

where the wall shear stress $\tau_w$ of the flowing liquid in a channel can be calculated with

$$\tau_w = \frac{\xi \cdot \rho_l \cdot \nu_l^2}{2}$$  \hspace{1cm} (2.7)$$

The liquid flows in a quadratic channel and thereby, the Fanning friction factor $\xi$ is given by [23]

$$\xi = \frac{14.3}{Re}$$  \hspace{1cm} (2.8)$$

The gas momentum force $F_m$ is dominated by the gas flow and was first assumed as a detaching force by Ramakrishnan [3]

$$F_m = A_n \cdot \rho_g \cdot \nu_g^2$$  \hspace{1cm} (2.9)$$

where $\rho_g$, $\nu_g$ are the density and the mean velocity of the gas phase, respectively. The detachment of the bubble is a highly dynamic process but can be assumed as a static phenomenon at the moment of the bubble snap-off. In that moment the retaining and detaching forces are in equilibrium:

$$F_{\text{retain}} = F_{\text{detach}}$$

$$F_{\sigma} + F_{sp} = F_d + F_{dl} + F_m$$

or, in detail:
This enables us to identify the key parameters to control the bubble generation with regards to the fluid properties which are determined by the employed chemical substances. Two groups of parameters can be identified: First, the velocity of the gas $v_g$ and the fluid $v_l$ can be varied, and second, the geometry of the nozzle opening defined by necking area $A_n$ and circumference $U_n$ takes an influence. The latter set of parameters is defined by the size and shape of the nozzle opening. This means that a design with specifically shaped nozzles allows to vary the bubble size without changing the mixing ratio through the volume flows or velocities, respectively. In the simplest case, the diameter of a circular nozzle correlates directly with the necking area of the liquid gas interface. In this case, the necking area $A_n$ and necking circumference $U_n$ can be calculated with

$$A_n = \pi \cdot \left( \frac{d_n}{2} \right)^2, \quad (2.11)$$

$$U_n = 2\pi \cdot \left( \frac{d_n}{2} \right)^2. \quad (2.12)$$

Hence, reducing the nozzle diameter results in a smaller necking interfacial area which consequently leads to a reduced bubble size. This can be seen in Figure 2-2 by the balancing forces $F_{\text{retain}}$ and $F_{\text{detach}}$ depending on the diameter $d_n$ of the round necking. The forces are calculated with the physical parameters for toluene and fluorine gas at 25 °C following Eq (2.10). These parameters were also used for the simulation model and are listed in Table 2-1. The results for the retaining and the detaching forces are plotted for four different resulting bubble diameters of 50 μm, 100 μm, 150 μm, and 200 μm. The detaching force $F_{\text{detach}}$ grows with the bubble diameter $d_b$, but is not influenced by the necking diameter $d_n$. However, with a decreasing necking diameter $d_n$ the retaining force $F_{\text{retain}}$ decreases quadratically. $F_{\text{retain}}$ does also fall with an increasing bubble diameter $d_b$. This different behavior has an impact on the balance of the forces in the moment of detachment. When the necking diameter $d_n$ gets smaller, the resulting bubble size $d_b$ has to decrease correspondingly.

In case of quadratic and rectangular nozzle orifices the resulting necking size is additionally influenced by the capillary forces of the liquid (see Figure 2-3). Due to surface tension liquid creeps along the corners inside the nozzle. Driven by the increased capillary pressure at the rectangular corners of the orifice, the gas liquid interface is pushed towards the horizontal center of the orifice. This enforces a necking already within the nozzle by moving the interface further out of the corners depending on the equilibrium contact angle. During the bubble generation, the circumference $U_n$ of the gas phase gradually

\[
\frac{4 \sigma}{d_b} A_n + U_n \sigma = \frac{1}{8} d_b^2 \pi \rho_l v_l^2 \left( 0.4 + \frac{24}{Re} + \frac{4}{\sqrt{Re}} \right) + 0.761 \frac{\tau_w d_b^3 \rho_l}{\eta_l} + A_n \rho_g v_g^2. \quad (2.10)
\]
2.2 Theory

declines, until the gas phase forms a cylinder inside the nozzle, surrounded by liquid protruding from the corners. According to the minimum surface energy the local bubble necking curvature $U_n$ can be determined with the Mayer and Stowe-Princen (MS-P) theory [24, 25]. This phenomenon is extensively discussed in the field of porosimetry and foam generation for oil recovery [26–29]. Recent research of Unsal et al [30] has shown that snap-off is the result of a dynamic capillary instability and happens inside the nozzle. This detachment inside the nozzle was numerically demonstrated for emulsification by

Figure 2-2: Plots of the retaining and detaching forces depending on the necking radius $d_n$ of a round nozzle. The necking radius is proportional to the circumference $U_n$ and the area $A_n$. The forces are plotted for four different resulting bubble diameters $d_b (50 \, \mu m, 100 \, \mu m, 150 \, \mu m, \text{and} 200 \, \mu m)$.

Table 2-1: Physical parameters of the fluids used for the graph in Figure 2-2 and in the CFD simulation at 25 °C [32].

<table>
<thead>
<tr>
<th>parameter</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>viscosity – toluene</td>
<td>$560 \times 10^{-6}$ Pa s</td>
</tr>
<tr>
<td>viscosity – fluorine</td>
<td>$22.6 \times 10^{-6}$ Pa s</td>
</tr>
<tr>
<td>density – toluene</td>
<td>866.9 kg/m$^3$</td>
</tr>
<tr>
<td>density – fluorine</td>
<td>3.15 kg/m$^3$</td>
</tr>
<tr>
<td>interfacial tension</td>
<td>$27.8 \times 10^{-3}$ N/m</td>
</tr>
<tr>
<td>(fluorine-toluene)</td>
<td></td>
</tr>
<tr>
<td>wall contact angle</td>
<td>$15^\circ$</td>
</tr>
<tr>
<td>(fluorine-toluene-silicon)</td>
<td></td>
</tr>
</tbody>
</table>
Kobayashi et al. [31] shows a rapid, time-depending shrinkage of the circumference until the neck is almost circular. Relating to these models of the neck transformation process we predict the size of the necking circumference $U_n$ by the nozzle geometry, as sketched in Figure 2-3. The necking circumference within a square-shaped nozzle decreases from an initial state, where only the corners are wetted, to an intermediate stable state and finally results in a cylindrical interface with diameter $d_n$ corresponding to the side length $a$. If the cross sectional area of the square expands, the necking circumference $U_n$ increases (Figure 2-3a-b). In comparison, the gas-liquid interfaces within rectangular nozzles are more predominantly influenced by the capillary effect and appear in a smaller circumference than in a square nozzle with similar cross sectional area, as shown in Figure 2-3b and Figure 2-3c. This illustrates that not only the cross sectional area of the nozzle opening changes the bubble necking effect, but also the shape and the aspect ratio of the nozzle orifice. Theoretically, a rectangular nozzle generates a much smaller necking area $A_n$ compared with the cross sectional area of the nozzle opening itself, and thereby, supports the detaching forces. Experiments, that will be explained in subchapter 2.5, show that the necking is additionally affected by the orientation of the unsymetric nozzles with respect to the liquid flow direction. For a rectangular nozzle with the narrow side in flow direction, as shown in Figure 2-3d, the neck is forced to one side of the opening by hydrodynamic forces. This will additionally reduce the necking circumference $U_n$.

In summary, this simple physical model shows that the size of a generated micro bubble
can be influenced by the nozzle opening and the fluid velocities, without changing the rheology of the fluids. For round nozzles the necking size depends directly on the cross sectional area of the opening. The MS-P theorem points out that the necking size and shape is influenced by the shape of the nozzle. On that account, when keeping the nozzle’s cross sectional area constant, the bubble size increases starting from a round, then square and finally rectangular shaped nozzle. Furthermore, the necking size depends on the nozzle orientation with respect to the liquid flow direction. Hence, the bubble size can be varied with the aspect ratio and the orientation of the nozzle without changing the rheology and velocity of the gas and liquid phase. The main issue of the following CFD simulations and experiments is to verify the influence of the nozzle geometry on the generated bubble size.

2.3 Nozzle geometry

To understand the generation of monodisperse micro bubbles, regarding to the presented physical model, a variety of different nozzle geometries was examined to show the influence of the nozzle geometry on the generated bubble size. In the model system, the liquid flows through a rectangular microchannel with a cross section of 300 μm × 300 μm. The gas is injected through a nozzle into the cross flowing liquid. The nozzle opening is positioned in the symmetrical center of one channel wall. Two different shapes of nozzle channels were examined as shown in Figure 2-4. A straight rectangular channel was fabricated in silicon with DRIE and an inverted and truncated pyramid-shaped nozzle was realized via KOH etching in silicon wafers with <100> orientation. Hence, the KOH nozzles have sloped side walls with an angle of 54.74° with respect to the wafer surface. Although the nozzles are very different, the nozzle openings of the KOH and DRIE nozzles were made identical. Different geometries were examined to analyze the influence of the aspect ratio of the nozzle opening on the generation of microbubbles. The first nozzle geometries have a square cross section (Q1: 20 μm × 20 μm; Q2: 40 μm × 40 μm). Two identical rectangular geometries have either the wide side (R1: 80 μm × 20 μm) or the narrow side (R2: 20 μm × 80 μm) orientated towards the flow direction of the liquid. All nozzle geometries and their orientations in the main channel are depicted in Figure 2-5.

2.4 Simulation

Computational fluidic dynamics (CFD) is a numerical simulation technique to model fluid flow in three dimensions, using the Navier-Stokes-equations. In order to investigate the bubble generation process, a three-dimensional model of the gas nozzle with the cross flowing liquid channel was established in CFD-ACE+ 2008.2 (ESI Group). We assume a gas-liquid system with laminar flow. The gas flows through the nozzle channel and is injected into a larger channel carrying the continuously flowing liquid. To calculate the approximate interface shape of the bubble, the volume of fluids (VOF) module was used. For the surface reconstruction, a piecewise linear interface construction (PLIC) was
Figure 2-4: Schematic illustration and a detailed view of (a) the straight DRIE etched channels and (b) the pyramid shaped KOH etched nozzles. The gray shaded area depicts the gas-liquid interface of a growing gas bubble at the nozzle tip.

Figure 2-5: Top view sketch of the different nozzle geometries and their orientations with respect to the flow direction of the liquid channel.
2.4 Simulation

applied. The transient calculation was controlled and automatically adjusted to match the Courant-Friedrichs-Lewy (CFL) number. This CFL number was set to 0.2, which limits the interface progress to only 20% of one cell per time step. Depending on the nozzle geometry and the fluid flow the simulation took 30 to 40 days CPU time on a Windows (XP Professional 64bit) personal computer with a Dual 3 GHz Intel Core2 processor with 8 GB RAM.

The behavior of the bubble formation was analyzed with images of the CFD-VIEW (ESI Group) post-processing software. Snap-off behavior and bubble generation frequency were analyzed with the extracted data files of the transient velocity and pressure conditions inside the channels for at least three consecutive bubbles. In assumption that the bubble has a spherical shape after detachment the bubble volume $V_b$ was used to calculate the resulting bubble diameter $d_b$. Moreover, the diameter can be determined with the gas volume flow $\dot{V}_{\text{gas}}$ and the bubble generation frequency $f_b$:

$$d_b = 3 \sqrt[6]{\frac{6}{\pi}} \cdot V_b = 3 \sqrt[6]{\frac{6}{\pi}} \cdot \frac{\dot{V}_{\text{gas}}}{f_b}.$$  \hspace{1cm} (2.13)

2.4.1 Geometry and simulation conditions

The used nozzle geometries for the CFD simulations are shown in subchapter 2.3. For the simulation model the nozzle opening is positioned in the symmetrical center of one channel wall and 300 μm behind the fluid inlet. The fluid channel ranging from the nozzle to the outlet is 1200 μm long. Only one half of the fluidic system was modeled, since the flows are symmetrical to the center plane of the channel and the nozzle. As explained before two different shapes of nozzle channels were examined (see Figure 2-4). A straight rectangular channel correlates with a fabrication with deep reactive ion etching (DRIE) and an inverted and truncated pyramid-shaped nozzle is obtainable by potassium hydroxide (KOH) etching in silicon wafers with $<100>$ orientation. All nozzle geometries and their orientations are depicted in Figure 2-5. In the simulation the DRIE model was meshed with 472'700 cells, while the KOH model has 311'000 cells. This number of cells represents the optimal mesh for the nozzle variations. A lower number of cells inhibits the simulation due to bad convergence of the simulation results. A higher number of cells does not change the aspirated data of the bubble snap-off but increases tremendously the computation time of the transient simulation. The reason is the VOF module that calculates maximum half of a cell length for the progress of a moving interface per time step. Considering that the fastest variance of the velocity of the phases is expected in the nozzle channel and at the outflow of the nozzle into the fluid channel, the grid was meshed finest in this region. The smallest cell has a cubic side length of about 3 μm and the largest cell at the liquid outlet has the cubic side length of 10 μm.

As previously mentioned, the microreactor is designed for a reaction of liquid toluene with pure fluorine gas. Therefore, toluene flows through the inlet of the liquid channel and
fluorine gas is injected through the nozzle. A parabolic velocity profile was generated at the inlet of both channels and the gas-liquid interface was flat at the start of all simulations. The pressure at the outlet was set to 100 kPa. All remaining geometrical boundaries, except the symmetries, were defined as walls. No-slip conditions were assumed at the walls. The wall contact angle for the gas-solid-liquid interface was set to 15° for all silicon surfaces. For all other physical data of the fluids at room temperature see Table 2-1.

### 2.4.2 Results

The bubble detachment in the CFD simulations is subdivided into three distinctive steps for all nozzle openings. Figure 2-6 depicts the time evolution for the rectangular DRIE nozzles R1 and R2. The characteristic shapes of the gas-liquid interface is shown exemplarily at the three time steps. The gaseous phase starts to inflate into the liquid phase which is depicted in Figure 2-6a. The bubble diameter gradually increases and a neck is formed inside the nozzle channel. Intrusion of liquid into the channel promotes the shrinkage of the necking area until a characteristic circumference of the gaseous phase is reached. At this time the circumference of the necking corresponds to a circle with the diameter which fits inside the cross section of the nozzle as shown in Figure 2-6b. After the formation of this characteristic neck shape the bubble snaps off after a specific time delay, depending on the nozzle aspect ratio and the orientation with respect to the liquid flow, see Figure 2-6c. For nozzles with the narrow side in flow direction, the cross flowing liquid supports the invasion of liquid into the nozzle and, consequently, the time between necking and snap-off decreases. This constriction of the gas bubble inside the gas channel and the subsequent snap-off due to capillary instabilities are distinctive characteristics for non-circular nozzles. Unsal et al [30] have experimentally shown the same characteristics in model pores and Kobayashi et al [31] have simulated these phenomena for emulsification with micro nozzles. Referring to the MS-P theory, the different nozzle openings show particular necking circumferences in the simulations and therefore result in different bubble sizes. This is shown in the simulation pictures in Figure 2-7. These qualitative characteristics are analogous for the KOH etched nozzles although the interfaces in the inverted pyramid channel look different due to the different geometry. The progress of the characteristic steps is described in detail by the pressure curve which is measured at the inlet of the nozzle channel. Figure 2-8 illustrates exemplarily the pressure development for the DRIE nozzles Q2, R1, and R2 at constant volumetric flow rates of gas and fluid phase with 1.04 ml/h and 97.2 ml/h, respectively.

The simulation is started with a flat gas-liquid interface inside the nozzle channel with 20 μm distance to the opening. For that reason, the first bubble detachment is not considered as valid for the determination of the bubble generation frequency. The geometry R1 shows the characteristic time step of bubble expanding for the second bubble and starts at $t = 1.57$ ms with a constant decrease of the pressure caused by the expanding bubble size to a minimum pressure of 2240 Pa. After this point the pressure increases
2.4 Simulation

rapidly as a result of the shrinking gas phase at the nozzle opening. The necking proceeds until the characteristic outline $U_n$ is reached ($t = 1.88 \text{ ms}$) and the pressure is pinned at around 3200 Pa. The bubble detachment occurs abruptly at $t = 2.8 \text{ ms}$ and the pressure curve reaches its maximum of 4646 Pa. Afterwards, the bubble formation is repeated periodically with a mean frequency of 700 Hz and an average bubble radius of 92.3 μm. The pressure profiles of Q2 and R2 are in principle identical, whereas the step of necking is less distinctive. Nozzle R2 shows an analog expansion phase like R1 with a shorter time

Figure 2-6: CFD simulation of the bubble generation for nozzle R1 (80 μm × 20 μm), as seen from the back respectively upstream side and for R2 (20 μm × 80 μm) from the side. The shaded area depicts the gas liquid interface. (a) The gas is expanding to a bubble. (b) Afterwards, the characteristic curvature of the necking is formed by the invading fluid until it reaches the maximum radius of a circle within the nozzle. This radius is the narrow side of the nozzle. (c) The bubble snaps off after a specific time and the steps recur periodically.
between the necking point \( t = 1.53 \) ms and the bubble detachment \( t = 2.17 \) ms and a maximum pressure peak of 4920 Pa. The necking phase of R2 varies with the next periods but stabilizes after seven bubbles. Hence, the bubble generating frequency for R2 \((1135 \text{ Hz})\) is 1.6 times higher than for R1, and the bubble radius of R2 \((78.5 \mu m)\) is smaller than R1 \((92.3 \mu m)\). The quadratic nozzle Q2 has a significant longer expanding phase \( t = 3.36 \) ms to a pressure minimum of 970 Pa. Necking and snap-off are at the same time \( t = 3.7 \) ms. The mean bubble formation frequency for Q2 is 274 Hz and a bubble radius of 126 \( \mu m \) is found.

All nozzle geometries were characterized for different gas and liquid flows by the pressure profiles extracted from the simulations. The measured frequency \( f_b \) was used to calculate the resulting bubble radius \( d_b \) with Eq (2.13). First, the bubble diameters of the DRIE nozzle geometries Q1, Q2, R1, and R2 were calculated for a variation of the liquid phase flow from 40 ml/h to 130 ml/h and a fixed volumetric flow rate of the disperse gas. The gas flow is fixed at 1.04 ml/h and the results are illustrated in Figure 2-9a. All measured minimum and maximum bubble diameters of each nozzle represent the regime limits for monodisperse bubbly flow. The graph shows decreasing bubble diameters with an increasing liquid flow rate. For the increasing liquid volume flow the difference between the nozzles R1 and R2 is observable in the graph. Comparing the nozzles Q2 and R1 with the same cross sectional area but different aspect ratio, there is a significant difference of the bubble diameter of 34 \( \mu m \) (27\%) at a liquid flow of 97.2 ml/h. At the same liquid flow, nozzle Q2 generates considerable smaller bubbles, of approximately 48 \( \mu m \) (38\%), than the rectangular nozzle R2 where the narrow side is in flow direction. The small square shaped nozzle Q1 produces approximately the same bubble size as nozzle R1 at a liquid
2.4 Simulation

Flow of 97.2 ml/h even though the nozzle opening is four times smaller. This correlates with the theoretical bubble size influenced by the MS-P circumference $U_n$ which depends on the small side of a rectangular nozzle. For the same conditions of fluid flow the nozzle R2 injects smaller bubbles and shows the influence of the liquid flow direction with respect to the nozzle opening. Further simulations with a fixed liquid flow rate and a variation of

Figure 2-8: Gas pressure at the nozzle inlet of the three DRIE geometries Q2, R1, and R2. The volumetric flow rates are constant at 1.04 ml/h (gas) and 97.2 ml/h (liquid).
the gas flow are depicted in Figure 2-9b. At a fixed liquid flow of 97.2 ml/h, the bubble diameter increase with increasing gas flow which is varied from 1.04 ml/h to 10 ml/h. For example, the bubble diameter of nozzle R1 increases from 92 μm at an 1.04 ml/h gas flow rate to 158 μm at an 10 ml/h gas flow rate. Although the bubble frequency growths linearly, the resulting bubble diameter does also increase with increasing gas flow as
predicted by Eq (2.13). For all simulations the bubble size can be scaled with the different nozzle shapes over the gas flow variation. On that account, nozzle R2 generates consistently smaller bubbles than nozzle R1. Furthermore, the resulting differences in bubble diameter get smaller for an increasing gas and liquid volume flow. This corresponds to the theory of force balance where the detaching forces increase with the increasing gas and liquid volume flow and the restraining forces stays constant. Hence, with increasing gas or liquid flow the influence of the necking circumference gets smaller and also the differences in the bubble diameter will decrease for all nozzles, see Eq (2.10). Finally, the simulation data of the different nozzle shapes show an influence of the aspect ratio and the nozzle orientation with respect to the direction of the cross flowing liquid. This is reflected by the order of the generated bubble sizes of the different nozzles. A nozzle with a rectangular shape (R1) injects smaller bubbles than a quadratic nozzle (Q2) with the same cross sectional area. The injected bubble sizes are even smaller when the rectangular nozzle has the narrow side in flow direction (R2).

The KOH etched nozzles Q2, R1, and R2 were simulated at a constant gas flow rate of 4.8 ml/h and 50 ml/h liquid flow rate, see also [33]. The rectangular nozzles R1 and R2 are also simulated at liquid flow rates of 97.2 ml/h, and 150 ml/h and show the same trends as the DRIE nozzles. The resulting bubble diameter of R1 decreases from 236 μm

![Figure 2-10](image-url)

**Figure 2-10:** Plot of the injected bubble diameter of the KOH nozzle geometries Q2, R1, and R2 for three different liquid flow rates with a fixed gas flow rate of 4.8 ml/h. The generated bubble diameter of DRIE nozzle R1, R2 are compared with the KOH nozzles at a liquid flow rate of 50 ml/h. At liquid flow rate of 50 ml/h the nozzles R2 (KOH), and R1, R2 (DRIE) are nearly the same with 134 μm, 135 μm, and 133 μm, respectively.
to 134 μm from the minimum to the maximum liquid flow rate. The nozzle R2, with the small side in flow direction, generates the smallest bubbles which decrease from a diameter of 216 μm at 50 ml/h to 121 μm at 150 ml/h liquid flow rate. In contrast to the DRIE nozzle Q2, the KOH counterpart generates smaller bubbles of 166 μm diameter than the rectangular nozzle R1 with 175 μm, at a liquid flow rate of 50 ml/h. Furthermore, the KOH nozzles show a behavior that is similar to the DRIE nozzles. In direct comparison at 97.2 ml/h liquid flow, the DRIE nozzles generate smaller bubble diameters than the KOH nozzles. For nozzle R1 the difference is between 175 μm (KOH) and 135 μm (DRIE). This is relatively large in contrast to R2 with 134 μm (KOH) to an almost identical value of 133 μm (DRIE). This indicates that the KOH etched nozzles show the same trends as the DRIE nozzles and equivalent bubble sizes except for the square nozzle geometry Q2.

The results of the CFD simulations show that the theoretical model can be used to predict the trends of the injected bubble sizes depending on the shape and orientation of the nozzle opening. The simulations demonstrate also an influence of the gas and liquid flows on the resulting bubble size. In theory as well as in the simulation the nozzle shape affects the bubble necking and therefore the resulting bubble size. This design parameter enables a scaling of the bubble size independent of the fluid flows. In addition, these effects are shown in more detail here for DRIE and KOH nozzles. These results therefore allow to pre-evaluate two general fabrication methods.

2.5 Experiments

The presented physical model and the simulations have shown the dominating parameters on microbubble generation. The aspect ratio and the orientation of the nozzle opening have a great influence on the frequency and bubble size without changing the rheology of the fluids. This was demonstrated in the simulations for two different nozzle fabrication methods, i.e. straight DRIE nozzles and truncated pyramid-shaped KOH nozzles. The two nozzle shapes show comparable characteristics for their monodisperse microbubble generation. In this section the design and fabrication of the two nozzle shapes is presented. The effect of the nozzle geometry on the generated microbubbles are verified in experimental tests. The nozzle variations are characterized by frequency and size of the generated microbubbles. Furthermore, measurements with varied gas and liquid flow rates are performed to investigate the characteristics of the realized bubble generators.

2.5.1 Device fabrication

For all experimental investigations simple fluidic test chips were fabricated in stacked silicon and pyrex wafers. The idea behind this concept is to achieve an optically transparent liquid channel with an silicon sidewall carrying the gas injection nozzle. The microfabrication process to produce the complete test chip with the two nozzle variations (DRIE, KOH) is schematically illustrated in Figure 2-11. The main channels in the liquid
layer are machined into a 500 μm thick pyrex wafer using a 300 μm wide saw blade with a depth of 300 μm, see Figure 2-11a. For a highly accurate positioning of the blade the saw lines are pre-patterned with a photolithographic step. The gas layer is machined in a 525 μm thick silicon wafer. It is covered on top with a thermally grown silicon oxide (SiO₂) etch mask of 1.5 μm thickness, see Figure 2-11b. A photolithographic step defines the gas channels. After opening the silicon oxide mask with RIE the gas channels are etched 50 μm deep with deep reactive ion etching (DRIE). The oxide etch mask is stripped subsequently with HF.

The nozzle layer is machined into a 525 μm thick silicon wafer with two different fabrication methods, see Figure 2-11c. For the KOH nozzles the wafer is masked at the front and back side with silicon oxide and silicon nitride (Si₃N₄). The silicon oxide is grown 300 nm thick by thermal oxidation. Over the oxide layer a 100 nm silicon nitride is deposited by low-pressure chemical vapor deposition (LPCVD). The back side of the wafer is photolithographically patterned to define the nozzles. The exposed silicon
nitride/oxide is etched with reactive ion etching (RIE) to open the etch mask. Afterwards the nozzles are etched with KOH from the back side through the silicon wafer to the etch stop at the front side. This etching step fabricates a wide opening of the nozzle channel at the back side and a small, defined nozzle orifice at the front. The silicon nitride/oxide mask is afterwards removed by wet chemical etching with hydrofluoric acid (HF). The DRIE nozzle fabrication is more complex and needs separate machining steps from the front and back side of the wafer. At the beginning, a 4 μm thick silicon oxide layer is thermally grown on the back side of the wafer and patterned with photolithography. After opening the oxide mask with RIE a buffer cavity is etched 400 μm deep into the silicon with a first DRIE step. The oxide mask is removed by HF etching and, thereafter, a new silicon oxide layer of 2 μm thickness is grown on the front side of the layer. As like for the back side the front side is patterned and the oxide mask is opened with RIE. Finally, the nozzle channel is etched 125 μm deep with a second DRIE step through the silicon to the buffer chamber and the oxide mask is removed with HF. Although the fabrication methods and the shapes of the nozzle channels are different, the orifices of the nozzle channels to the main channels were made in the same size and show comparable geometric variations of ±2 μm.

The fabrication process of the fluidic test chip is completed by bonding the three functional layers, see Figure 2-11d. The front of the gas channel layer is connected to the back side of the nozzle layer via silicon fusion bonding before the pyrex wafer is anodically bonded with the main channels facing the front side of the nozzle layer.

The chips have outer dimensions of 2 cm × 2 cm and carry three main liquid channels, each channel equipped with one nozzle opening on its bottom side. These straight main channels have a cross section of 300 μm × 300 μm and are machined in pyrex to allow an observation of the bubble generation through the nozzle. The silicon nozzle layer is connected with a 50 μm deep gas channel fabricated in silicon. Figure 2-12 shows a picture of a complete fluidic test chip and a micrograph cross section through a DRIE and a KOH nozzle.

The straight nozzle channels, fabricated with deep reactive ion etching (DRIE), are 125 μm long and lead to a buffer chamber with a 500 μm × 500 μm quadratic size and 400 μm depth (indicated in Figure 2-11c). This cavity connects the nozzle channel to the gas supply channel. The nozzle channels, etched with potassium hydroxide (KOH) in <100> silicon wafers, are etched through the wafer and therefore 525 μm long. As a consequence of the silicon crystal orientation the nozzle channel has sloped side walls with an angle of 54.74° with respect to the wafer surface. This facilitates the coating with an inert nickel layer for the further use of the nozzle structure for direct fluorination, see chapter 5. Furthermore, the KOH etching of silicon is a low-cost method and features well-defined corners and edges which are important factors for the behavior of two-phase flows in microstructures. For more details see [33].
2.5 Experiments

2.5.2 Measurement setup for bubble observation

The setup for the bubble generation experiments is shown in Figure 2-13. It consists of the fluidic test chip mounted in a chip carrier, a syringe pump to feed the continuous liquid phase and a mass flow controller for the gas flow. The chip carrier was developed within the working group, see [34, 35]. The syringe pump was an Injectomat 2000 (Fresenius, Germany) and the mass flow controller was an El-Flow F-200CV (Bronkhorst, Netherlands). Both were connected to the inlets of the chip carrier. Bubble formation was observed through a BX51 (Olympus, Japan) microscope with a pco.1200 (PCO, Germany) high speed camera. The camera works with an exposure time of 245 μs, which results in a
frame rate of 4081 Hz for an image frame of 610 × 142 pixels. All pictures were analyzed with the software pco.camware x64 (PCO, Germany). This high speed camera measurement setup was developed during the bachelor thesis of Herbstritt, see [36]. For a more precise detection of the bubble frequency over a long time, a photodiode with a high response frequency of 14 kHz (OPT101, Texas Instruments, USA) is mounted to the microscope. The OPT101 is a photodiode with an on-chip transimpedance amplifier and the output voltage increases linearly with the light intensity. Figure 2-14 shows the circuit diagram of the photodiode with the amplifier. It is connected to a power supply (HM8143, Hameg Instruments, Germany) with a voltage of 5 V. The voltage output is detected with a voltmeter (NI 9215, National Instruments, USA). Through the same con-focal axis the light of a halogen lamp is focused on the bottom of the liquid channel 2 mm downstream of the nozzle. These irradiations are reflected on bottom surface of the silicon channel and guided through a pinhole to the photodiode. With the magnification of the microscope and the constriction of the pinhole, the photodiode detects variations of the reflected light intensity solely over a round area of 10 μm diameter. Considering that this detection area is significantly smaller than the bubble size the intensity of the detected light changes with...
2.5 Experiments

a bubble passing through the detection area. Therefore, the voltage output of the photodiode changes periodically which is measured with the voltmeter and analyzed using a programmed virtual instrument (Lab-View, National Instruments, USA) in combination with Matlab (MathWorks, USA). Figure 2-15 shows a picture of the measurement setup and a detailed view of the microfluidic chip in the chip carrier.

![Figure 2-14](image1.png)

**Figure 2-14:** Photodiode OPT101 with on-chip integrated transimpedanz amplifier.

![Figure 2-15](image2.png)

**Figure 2-15:** This figure shows a picture of the (a) fluidic setup for bubble detection and a detailed view of the fluidic carrier with the microfluidic chip.

The presented measurement setup was combined with a heating element to determine the bubble generating frequency at higher temperatures. This is schematically shown in Figure 2-16. The chip carrier (see also Figure 2-13) has an opening underneath the chip as like from the top. The microfluidic chip was thermally contacted through this opening with a copper block and thermal compound to a thermoelectric Peltier heater (QC-127-1.4-3.7MS, Quick-Ohm, Germany). The Peltier heater was controlled by a
voltage source (HM8143, Hameg Instruments, Germany) and the temperature was measured in the copper block near the chip with a thermo element (Type T, Labfacility, UK), connected to a voltmeter (NI 9219), and was analyzed using a programmed virtual instrument (Lab-View). Due to the low height of the setup, it can be placed under the microscope for the bubble frequency detection. The microfluidic chip is thermally isolated with the pyrex cover on top, the chip carrier (PEEK) and the gasket (silicone).

To assure non-hazardous experimental conditions 2-propanol was used as continuous phase and nitrogen gas as dispersed phase instead of toluene and fluorine gas. These substances show comparable fluidic behavior for a two-phase flow system at room temperature. This was tested in measurements that compare 2-propanol and toluene for bubble generation in the microchannel. The liquid flow rates were 50 ml/h and 97.5 ml/h with variations of the nitrogen gas flow rate between 20 ml/h and 60 ml/h. The maximum difference of the measured bubble sizes between 2-propanol and toluene were 4%.

2.5.3 Measurements

Videos were taken and analyzed to understand the process of monodisperse bubble formation and to determine the bubble generation frequency. Figure 2-17 illustrates the bubble size and shape for the KOH nozzle Q2 for a constant liquid volume flow and three different gas flows rates of 19.5 ml/h, 26 ml/h, and 35.5 ml/h. With increasing gas flow rate the bubble frequencies rise and the size of the bubbles expands. The image analysis shows that the bubbles are spherical in shape which correlates to simulation results of perfectly spherical bubbles (see subchapter 2.4). In all experiments the generated bubbles did not stick to the channel surface. This is characteristic for microfluidic systems where surface forces dominate gravitational and inertial forces, which is reflected in small Bond

Figure 2-16: Schematic illustration of the measurement setup for the bubble generation with different temperatures. The microfluidic chip is heated with a thermoelectric peltier element and contacted with a copper block and thermal compound.
2.5 Experiments

and Weber numbers of this system ($Bo \ll 1$, $We \ll 1$), see also subchapter 1.4.1. The measurement of the bubble diameter cannot be done with the required accuracy due to a limited depth of focus and deep shadows of the microscope light. Furthermore, the measurements from the video pictures represent only a short time period. However, with the assumption that the bubbles are spherical and that no leakage of gas is happening, the bubble diameter $d_b$ can be calculated with the bubble volume $V_b$, obtained from the frequency $f_b$ and the gas volume flow rate $\dot{V}_{gas}$, see Eq (2.13).

The average of the measured frequency was calculated from three different 100 ms long videos taken with five minutes of delay. The comparison of the measured diameter from the videos and the diameter calculated from the frequency show corresponding dimensions.

For frequency analysis over a long-term period the already presented photodiode measurement setup was used. These measurements were done over a period of 1 s and measured with a sampling rate of 10 kHz. The monitored periodic voltage curves were analyzed for the maximum peaks which represent the most reflected light and thereby the area between two bubbles. With a fast Fourier transformation (FFT) the repetition frequency of the monodisperse bubbles was obtained. This measurement was repeated 10 times with 5 s delay between every step. The mean value of the obtained frequencies was calculated whereby only a maximum variance of 2% was allowed. Otherwise the measurement was not considered as valid because the bubbles would not be monodisperse in these cases. Figure 2-18 shows exemplarily a monitored periodic voltage curve and the frequency plot after the FFT. The monodisperse bubble were generated with a 40 μm × 40 μm KOH nozzle with a liquid flow rate of 97.2 ml/h and a gas flow rate of 32.4 ml/h. The frequency plot shows the maximum peak and therefore the bubble frequency at 3 kHz which results in a bubble diameter of 179 μm.

Figure 2-17: Sequence of the generated bubbles for KOH nozzle Q2 (40 μm × 40 μm) with constant liquid flow at 50 ml/h and gas flow of (a) 19.5 ml/h, (b) 26 ml/h, and (c) 35.5 ml/h. The generated diameter are (a) 199 μm, (b) 214 μm, and (c) 222 μm. The channel width is 300 μm and the black stripes are shadows of the channel walls.
For the measurements of the resulting bubble diameters, different experiments were made at constant gas flow with variation of the liquid flow rate and at constant liquid flow with gas flow variation. The nozzle channel shapes DRIE and KOH were investigated with the described geometric variations Q2, R1, and R2. For these experiments, the small quadratic nozzle Q1 was not considered because it showed non-tolerable geometric inaccuracy. Furthermore, the small nozzle shows a tendency for clogging and is thus not reliable. The frequencies had only maximal variations of ±2% which displays the high degree of monodispersity. All frequencies were determined with increasing and decreasing gas or liquid flow rates and no hysteresis effects were detected. The measured minimum and maximum diameters of each nozzle represent the regime limits for monodisperse bubbly flow.

2.5.4 Results

The first series of experiments investigates the bubble formation frequencies of the different nozzle geometries for a variation of the liquid flow at a constant gas flow rate, see also [33, 36]. The gas flow was fixed at 32.2 ml/h while the liquid flow was varied between 40 ml/h and 100 ml/h. The results for the DRIE and KOH nozzle channels are illustrated in Figure 2-19. For all nozzles, the bubble diameter decreases with increasing liquid volume flow. Every nozzle variation generates bubbles in a specific range of the liquid volume flow. Among all designs the quadratic DRIE nozzle Q2 injects the smallest bubbles for a liquid flow rate between 60 ml/h and 97.2 ml/h where the bubble diameter decreases from 197 μm to 175 μm, respectively. The rectangular DRIE nozzle R1 generates significantly larger bubble diameters from 245 μm to 209 μm between 50 ml/h to 90 ml/h liquid volume flow. The bubble diameter obtained with the DRIE nozzle R2 shows similar bubble diameters as DRIE Q2, with 187 μm at 70 ml/h and 176 μm at 97.2 ml/h.

Figure 2-18: This figure shows (a) the AC part of the periodic voltage signal of monodisperse generated bubbles and (b) the frequency plot after the FFT. A 40 μm × 40 μm KOH nozzle generated the bubbles with a liquid flow rate of 97.2 ml/h and a gas flow rate of 32.4 ml/h.
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the DRIE nozzles, the KOH nozzles shows two separated regimes of monodisperse bubble generation with a chaotic area in between. The first regime is between 40 ml/h and 60 ml/h and followed by the chaotic region where no monodispersity is obtained. After this region, each nozzle starts to generate bubbles with considerably smaller diameters at a specific liquid flow rate. For example, the KOH nozzle R2 starts to produce bubbles at 40 ml/h liquid flow rate with 236 μm diameter which decreases to 225 μm at 55 ml/h liquid flow. With increasing liquid volume flow, the nozzle generates no monodisperse bubbles up to a liquid flow of 75 ml/h. At this point the regime changes and the injected bubble diameter of this nozzle is 197 μm and decreases to 181 μm at 97.2 ml/h. The quadratic KOH nozzle Q2 generates slightly smaller bubbles than the rectangular KOH nozzle R2 with the narrow side in flow direction, and KOH nozzle R1 generates the biggest bubbles. The difference between the bubble diameters is considerably larger at low liquid volume flow rates but becomes smaller with increasing liquid flow rate. In general, the KOH nozzles show comparable bubble diameters to the corresponding DRIE nozzles for a variation of the liquid flow. For the DRIE nozzles the ascending order of the nozzles is given by the size of the generated bubbles and therefore R2, Q2, and R1. Hence, the rectangular nozzle with the narrow side in flow direction generates the smallest bubbles, followed by the quadratic nozzle and the rectangular nozzle R2 with the wide side in flow direction. This is in contrast to the KOH nozzles which have an order of Q2, R2, and R1 judging again from the ascending bubble size. For both, DRIE and KOH nozzles, a dependence of the generated bubble size on the nozzle orientation to the liquid volume flow is obvious. The

Figure 2-19: Comparison of DRIE and KOH nozzles for the variation of the liquid flow rate with constant gas flow rate of 32.2 ml/h.
distinctive bigger bubble sizes for quadratic nozzles, found in simulations, could not be confirmed for the experimentally tested KOH nozzles. However, the simulations were done at a smaller fixed volume gas flow of 4.8 ml/h and therefore a switch of the physical regime cannot be excluded. The experimental setup shows its limits at gas flows smaller than 16 ml/h. This originate from standard deviations of the mass flow controller for the gas and the syringe pump for the liquid. These standard deviations plus the fluidic capacitance of the supply tubing to the chip gain influence for small gas flows and no monodisperse bubbles were generated.

Following the tests with a constant gas flow, experiments with a constant liquid flow of 97.2 ml/h were done, as illustrated in Figure 2-20. The gas flow rate is varied between 16 ml/h and 60 ml/h and shows increasing bubble diameters for all nozzle geometries. Although the measured frequency increases linearly, the resulting bubble diameter increases with increasing gas flow, see Eq (2.13). The results from the DRIE nozzles are depicted in Figure 2-20a. Here, the quadratic nozzle DRIE Q2 shows a linearly increasing bubble diameter from 151 μm at 16 ml/h to 183 μm at 39 ml/h gas flow rate. With higher gas flow rates a chaotic area is developed until another monodisperse regime occurs. This regime starts at 42 ml/h with a bubble diameter of 207 μm and ends at 60 ml/h with a diameter of 227 μm. Nozzle DRIE R1 shows an increasing bubble diameter, from 185 μm to 213 μm at 36 ml/h and 60 ml/h gas flow rate, respectively. The excursion at 26 ml/h with a 189 μm bubble diameter may indicate some other flow regime change. From 16 ml/h to 40 ml/h gas flow rate the quadratic nozzle of Q2 generates the smallest bubbles, closely followed by the rectangular nozzle R2 and then, with slightly larger bubble diameters, R1. However, the same nozzle Q2 injects the biggest bubbles within its second regime. The KOH nozzles exhibit bubble diameters comparable to the DRIE nozzles but all three nozzle geometries show a switch of their monodisperse bubble generation regime. The most distinctive monodisperse regime of KOH Q2 ends at 42 ml/h, for the rectangular KOH nozzles R1, R2 this happens at 45 ml/h. A chaotic area is following for higher flow rates with no monodispersity. Thereafter, the nozzles start to generate monodisperse bubbles again at a significantly higher diameter than before. Nozzle R2 shows already the first change of the regime at gas flow rates of 23 ml/h and 32 ml/h. First, the nozzle produces bubbles with larger diameters and switches, after the chaotic area, to smaller bubble diameters. A similar change of the bubble generating regime is also probable at a runaway value of KOH R2 at 19 ml/h gas volume flow.

The DRIE and KOH nozzles show comparable results for increasing gas flow. For a direct comparison of the DRIE and KOH nozzles Figure 2-21 shows a detailed graph for a gas volume flow from 28 ml/h to 40 ml/h gas volume flow. This is a common central monodisperse bubble regime for all nozzles. Within these gas flow rates nozzle DRIE Q2 shows the smallest bubble diameter, followed by the rectangular nozzle DRIE R2 and then the quadratic KOH Q2. The DRIE R2 nozzle and the two rectangular KOH nozzles R1, R2 change the ascending order but differ at mostly 2 μm (1%) of the bubble diameter. For this regime the quadratic nozzles generate smaller nozzles than the rectangular nozzles with
the appropriate nozzle channel shape (DRIE or KOH). The rectangular nozzles R2 with the narrow side in flow direction inject smaller bubbles than the R1 nozzle counterpart with the wide side in flow direction. In this regime, the ascending order of the nozzle geometries by the bubble diameter is Q2, R2, and R1 for DRIE and KOH nozzle shapes.

**Figure 2-20**: The graphs show the diameter measurements of (a) DRIE and (b) KOH nozzles at a constant liquid volume flow rate of 97.2 ml/h. At a gas flow rate of 19 ml/h the KOH nozzles R1 and R2 have nearly the same bubble diameters of 184 µm and 183 µm, respectively.
For the monodisperse regimes with higher gas volume flows of approximately 45 ml/h the ascending order is changed to R2, R1, and Q2. In contrast, the predicted order of the nozzles from theory and simulations is R2, R1, and Q2. This means that the experimentally measured ascending order of the nozzle geometries is only partly comparable with the order examined with theory and simulations. Therefore, it is important to define the fluid flows of interest for a precise characterization of the geometries.

The measurements to determine the bubble diameters at higher temperatures were done with the rectangular KOH nozzle R2 (20 μm × 80 μm). The bubbles were analyzed at 26 °C and at 30 °C. The graph in Figure 2-22 compares the bubble diameters of the two temperatures with a constant liquid volume flow rate of 97.2 ml/h and a gas flow rate variation between 20 ml/h and 60 ml/h. The generated bubbles show the same trends of increasing diameters between 22.7 ml/h and 42 ml/h and followed by a chaotic regime. At 55 ml/h gas flow rate follows a new bubble generating regime. The trend of the bubbles at 30 °C are the same as for 26 °C but with slightly larger diameters of approximately 4%. This means that the temperature difference has a bigger effect on the retaining forces than on the detaching forces as presented in subchapter 2.2, Eq (2.10).

The results of the simulations and the experiments cannot be compared directly because the simulations were done at generally lower fluid volume flows. The constant gas volume flow was fixed at 4.8 ml/h instead at 32.2 ml/h like in the experiments. Even though, the constant liquid volume flow was fixed at 97.2 ml/h for the simulation as like for the
experiments, it was impossible to characterize the nozzles for the same gas flows. The experimental setup shows its limits at gas flows smaller than 16 ml/h. These problems originate from standard deviations of the mass flow controller for the gas and the syringe pump for the liquid. These standard deviations plus the fluidic capacitance of the supply tubing to the chip gain influence for small gas flows. Moreover, the simulations of gas flow rates higher than 10 ml/h requires a significantly longer computing time than the simulations for lower gas flows. Therefore, it was not feasible to perform the simulations for higher gas flows considering that the computing time for the lower gas flows were already at 30 to 40 days on a 64 bit personal computer with a Dual 3 GHz Intel Core2 processor with 8 GB RAM.

However, on basis of the obtained results, a difference of the generated bubble sizes between the nozzle geometries is detectable. This geometric variation of the nozzle represents an additional degree of freedom for the generation of monodisperse microbubbles inside a laminar liquid flow, independent from rheology and flow rate of the fluids. The characteristics of the frequency shifts denote a limit of the bubble generating regime from lower to higher gas flow rates. We have also investigated a bifurcation [16] in the chaotic area between the two regimes, with a corresponding bistable frequency of bubble generation between the lower and upper regime. The observed bifurcation and the regime shifts could have the reason in the experimental error sources of the deviating fluid controls which correlate with the fluidic capacitance in a negative way. On the other hand, the bubble generating regime change can also be a change of the physical process of the

**Figure 2-22:** This graph shows the diameters of the KOH nozzle R2 for the temperature of 26 °C and for 30 °C with a constant liquid volume flow rate of 97.2 ml/h. The maximum difference between the two temperatures are maximum 2%.
2 Bubble generation

detachment mechanism from the nozzle to a jetting bubble snap-off inside the liquid channel [37]. This was not detectable with the current experimental observation from the top of the nozzle opening. These chaotic regimes were not detected in the simulations because they represent perfect volume flows with no capacitances in supply tubings and ideal boundaries. The volume flow rates for the simulations are to small to induce a change of the detachment mechanism to a jetting in the liquid channel [37].

2.6 Conclusion

A theoretical treatment for the phenomena of bubble detachment of microbubbles in a cross flowing liquid has led to a physical model with an equilibrium of the retaining and detaching forces in the moment of bubble snap-off. This physical model allows to identify the most important influence parameters. These parameters are not only the medium characteristics, the fluid velocities or the size of the nozzle openings but also the aspect ratio of the nozzle openings and their orientation with respect to the fluid flow. This influence of the geometry on the generated bubble size was the main aspect that was proven with the simulations and the experiments.

The theoretical result of the influence of the nozzle geometry were determined in three dimensional CFD simulations for two kinds of possible fabrications methods. These methods are the fabrication with DRIE which results in straight nozzle channels and the fabrication with KOH etching which results in inverted and truncated pyramid-shaped nozzle channels. The simulations demonstrated a new nozzle concept of rectangular nozzles for the generation of monodisperse microbubbles which is necessary for an effective direct fluorination in a microreactor. The results of the different nozzles show that the aspect ratio of the nozzle opening has an important role for the generation of microbubbles. Rectangular nozzles generate smaller bubbles with higher frequencies than quadratic nozzles with the same cross sectional area. Furthermore, it was discovered that the orientation of the rectangular nozzles with respect to the liquid flow direction has a major effect on bubble size and generating frequency. Hence, the nozzle geometry with the narrow side in flow direction exhibit the smallest bubbles. These effects were also observed with a variation of the gas and liquid flow.

This novel rectangular nozzle concept of the presented theory and CFD simulations was verified with experimental tests. It was possible to produce the nozzles with DRIE and with a low cost KOH etching process. With both fabricated nozzles, measurements with varied gas and liquid flow feature a linear scaling of the bubble size within separated regimes. Moreover, the experiments show also that the aspect ratio and not only the cross sectional area of the nozzle is a dominant scaling factor for the monodisperse generation of microbubbles. As like in the simulations, shows the orientation of the rectangular nozzles with respect to the liquid flow direction an sufficient influence on the generation frequency and the resulting bubble diameter. This applies for both fabrication methods of DRIE with straight nozzles and KOH with truncated pyramid-shaped nozzles. The size and the
frequency of the generated bubbles of the DRIE and KOH nozzles are comparable. However, the KOH nozzles are preferable due to the sloped side walls of the KOH nozzles. They facilitate a workable coating of the nozzle with an inert nickel layer for further use in the direct fluorination microreactor.

2.7 References

2.7 References


3 Fluorine resistant materials and fabrication methods

3.1 Introduction

An ongoing development of micromachining technologies within the microelectronic and microelectromechanical system (MEMS) industry has advanced the fabrication possibilities of microfluidic systems [1]. From the beginning around 1975 with gas chromatographic chips [2] and the commercial production of inkjet printheads [3], microfluidic devices were developed for a broad range of applications. Today, micromachined microfluidic systems include micro heat exchangers for integrated circuit (IC) chips, micropumps for medical implants, flow and pressure sensors, chemical detectors, and complex systems for the automation of analytical chemistry [1]. Miniaturized total analysis systems (μTAS) combine pumps, valves, separation channels, flow sensors, and chemical detectors with a complex fluidic handling system in one single chip [4]. All these applications have particular requirements for the functional materials. Therefore, micromachining processes were further developed from silicon to a broad range of materials like glass, quartz, polymers and also metals [5].

Another challenging field of microfluidics is microreaction technology, which also combines different microfluidic and sensor devices into one chip. Miniaturization of chemical reactors provides innovative advantages for the chemical, petrochemical and pharmaceutical industry [6, 7]. The main benefits are the improved selectivity and the enhanced control of chemical reactions [8–10]. This is possible due to the downscaling into micrometer dimensions, where large interface areas and a high heat and mass transfer are achievable. The use of these effects allows to run chemical reactions under much more aggressive conditions than in conventional reactors [11]. Additionally, MEMS offers a way to integrate control, sensing, and reactor functions in one device via monolithic or modular fabrication concepts [12]. With these capabilities microreactors enable reaction pathways which were previously not feasible in conventional reactors, like, for instance, the direct fluorination of liquid solvents [13–15].

The overall aim of the here presented research is a new multiphase microreactor concept for the direct fluorination of aromatic molecules. This reaction sets particular and ambitious requirements for mixing, heat exchange, a hermetically tight sealing, and a high chemical resistivity of the wetted materials due to the hazardous nature of fluorine gas.

The reaction needs a proper and fast mixing of solvents to assure homogeneous reaction conditions. Three-dimensional (3D) meander microchannels implement chaotic advection to passively enhance fluid mixing compared to two-dimensional (2D) structures [16, 17].
Although 3D structures show better conditions for a rapid mixing than 2D structures (see subchapter 6.2), they are seldomly used due to limits of conventional microfabrication technologies. The enhanced mixing via turbulent flow, obtained in a 3D geometry will also enhance the heat conduction from the fluid into the surrounding channel walls. Hence, 3D channels would be advantageous in two ways, as they provide enhanced mixing and heat transfer at the same time.

The heat transfer in the channel wall as well as a tight sealing and chemical inertness for chemical microreactors is ideally solved by using a metal as a base material. Metals are known for their good heat conduction and allow a hermetic encapsulation [1]. The direct fluorination with fluorine gas and hydrogen fluorine as reaction product require specific corrosion-resistant materials. Only a few metals are corrosion resistant against both reactants. These include platinum, palladium, gold, nickel and nickel alloys (especially Monel) [18, 19]. Metal microchannels can be fabricated by micromilling, etching or laser machining into the metal substrate [12]. For a mass production with microfabrication techniques, selective electroplating can be used. For this process, a patterned photoresist covers partially a metal seed layer. The open spaces are filled with metal in an electroless or electroplating process and the photoresist is removed afterwards. For microchannels with higher aspect ratios, it is possible to use the LIGA or UV-LIGA process. This process is based on a combination of synchrotron or ultraviolet (UV) radiation lithography, electroforming and micromolding (in German: Lithographie, Galvanoformung, Abformung) [20]. However, all these fabrication methods will only create open channels on a substrate that have to be covered to seal the metal microchannels. The group of Joo et al. solved the sealing problem with a two step electroplating process [21]. First, an electroplating step is performed until the patterned photoresist is almost covered, followed by a subsequent removal of the photoresist through the remaining gaps. Second, the electroplating is resumed until the channel is closed. In the work of Papautsky et al. the metal microchannels are formed as pipes on the substrate surface [22]. The fabrication starts with an electroforming of the channel bottom wall. Afterwards, the hollow lumen dimensions are defined by a thick photoresist as a sacrificial layer. The channel side and top walls are electroplated and the sacrificial layer is removed subsequently. This fabrication method allows the formation of micropipes with thin walls on top of a substrate. If required the micropipes can be released afterwards. However, the dimensions are still limited by the sacrificial photoresist thickness and the time-intensive removal thereof, after the electroplating. A new approach for metal deposition is electroless plating inside a microchannel [23, 24]. A microchannel is formed in polydimethylsiloxane (PDMS) and sealed against the substrate of interest. The electrolyte solution is pumped through the channel and the metal deposits on the substrate. However, this method forms only thin films of approximately 1 μm on a surface instead of metal microchannels. This metallization technique can be used to electrolessly plate complete channels with cross sections down to a few micrometers as shown by Heuck et al. [25]. In their work they performed the electroless plating inside a micromachined silicon oxide channel to deposit silver electrodes at the sidewalls.
Again, all presented microfabrication techniques are limited to 2D, and except the method of Heuck et al. are restricted in their dimensions by the sacrificial layers in use. Furthermore, only the method of Papautsky et al. is used to release the micropipes from the substrate. These fabrication technologies do therefore not allow the realization of freestanding micropipes with a true 3D geometry. Such freestanding 3D micropipes could be surrounded by a flowing coolant which would increase the heat conduction, and decrease the response time upon variations of the temperature inside.

In this chapter, we present the material tests for plated metal that can resist fluorine gas. Furthermore, a fabrication process is presented to obtain 2D, 2½D and 3D embedded or freestanding metal micropipes. This patent-pending process [26] is based on conventional micromachining and electroless nickel plating inside a microchannel of structured and stacked silicon substrates. The post-formed nickel microchannel resists an etching with KOH which facilitates to fabricate freestanding, functional micropipes. These embedded or freestanding micropipes can be machined with a broad range of aspect ratios and the channel wall thickness depends only on the electroless plating time. The material strength of electroless plated nickel micropipes was analyzed.

For the microreactor only 2D microchannels, fabricated via in-channel electroless plating, are required. However, the nozzle for the gas bubble injection is a structure in the third dimension relative to the 2D microchannel. With the technique to release the microchannels from the silicon substrate it is possible to determine the quality and the gas tightness of the deposited nickel layer. That are crucial factors for the application in the microreactor. In addition to these requirements of the microreactor, the fabrication method of 3D, freestanding micropipes provides numerous new applications. That is demonstrated with two applications in chapter 6. This is on the one hand the enhanced mixing quality of 3D mixing microchannels and on the other hand the improved heat transfer capability of free-standing microchannels.

### 3.2 Fluorine resistant materials

For the further application of the nickel micropipes in a microreactor, several plated metals were tested as a chemically resistant passivation layer of the silicon substrate against chemical attack of the fluorine gas. Thin metal layers can show pinholes and the metal plating can have small defects at edges and corners of the etched microchannel with high aspect ratios [27]. Through this pinholes or defects, fluorine gas can penetrate the underlying substrate and start to etch the silicon. Therefore, metal layers were deposited with different layer thicknesses on structured silicon with minimum features of a 50 μm width and a 300 μm depth. The silicon chips were examined after the metalized surfaces were exposed to fluorine gas to detect any penetration of the metal passivation layer and the underlying silicon. In addition, the metal surfaces were analyzed for their surface composition by x-ray photoelectron spectroscopy (XPS).
3.2 Fluorine resistant materials

3.2.1 Test setup

For the material tests of several plated metal layers against fluorine gas, structured silicon chips were used as a substrate. The silicon chips were machined with deep reactive ion etching (DRIE) to fabricate different micro structures. This fabrication method is explained in detail in the following subchapter 3.3. The structures were microchannels with different aspect ratios with a common depth of 300 μm and a width of 100 μm, 300 μm, 500 μm, 700 μm, and 900 μm, respectively. The test chip with outer dimensions of 2 cm × 2 cm is shown in Figure 3-1a after an exposure to fluorine gas. The test chips had straight and meander-formed microchannels. Therewith, it was tested which channel form and which structured feature withstands the fluorine gas in the best way, as exposed protruding features may provide an attack point for fluorine, depending on their shape and hence metal coverage. Moreover, the IMTEK logo at the bottom of the chip featured high aspect ratios from 50 μm width to 300 μm depth and is therefore a critical part for a complete metallization. The structured silicon chips were covered with a vapor-deposited palladium seed layer. This layer was deposited in a thickness of 150 nm. After a rapid thermal annealing (225 °C, 3 min) a palladium silicide interface is formed between palladium and silicon. This features an excellent adhesion of the seed layer to the silicon substrate [28]. The palladium surface was cleaned to remove the surface oxide layer immediately before the metal plating. This pretreatment was a hot electro-degreasing in sodium hydroxide (0.3% concentration, 75 °C, 10 s) and an acid pickling with hydrochloric acid (38% concentration, 50 °C, 30 s, and ultra sound). Electroplated gold (Puramet 202, AMI-Doduco, USA) and nickel (Slotonik 50, Schloetter, Germany) were...

Figure 3-1: (a) Test chip (2 cm × 2 cm) for the fluorination test with minimum channel width of 100 μm. The gold-bronze color and the grains on the surface are caused by the fluorination.
tested as passivation layers against fluorine gas. Therefore, different metal layers were plated on the structured chip surface. The electrolyte temperatures during electroplating were either 58 °C for Puramet 202 or 55 °C for Slotonik 50. The metal layers differed mainly in their thickness of 6 μm, 12 μm, and 16 μm. Each layer thickness was plated with three different current densities during electroplating of 30 mA/dm², 40 mA/dm², and 50 mA/dm², respectively. Different current densities have an effect on the grain size within the metal layer and generate different electric fields on the chip surface. This can affect the electroplating in edges and corners of the microstructures and thus the step coverage of the protruding features via the dog bone effect [29]. Moreover, electroless plated nickel (SurTec®833, SurTec, Germany) was tested for its chemical resistivity in fluorine gas. The 16 μm thick nickel layer was plated with a deposition rate of 6 μm/h at a temperature of 92 °C and a pH-value of 4.8.

The test chips were placed in a chip carrier, where only the metalized chip surfaces were exposed to the fluorine gas during the test, see Figure 3-2. The carrier was placed inside an autoclave made of Monel that can be filled with fluorine gas. The fluorination tests were performed by our project partners at the Laboratory of Molecular and Coordination Chemistry, University of Freiburg. The subsequent XPS measurements were done by the Laboratory for Chemistry and Physics of Interfaces, University of Freiburg.

![Figure 3-2](image_url)

**Figure 3-2:** This figure shows the chip holder for the fluorine resistivity tests where only the structured and metalized surface is exposed to the fluorine gas. (a) Picture of the top and the bottom of the chip holder with the test chip. (b) The schematic cross section of the chip holder shows the position of the test chip between the gaskets.

### 3.2.2 Measurements and discussion

**Electroplated gold and nickel**

The metal-covered chips were tested with 100% fluorine gas at a pressure of 1 bar for 6 h. All gold layers did not protect the underlying silicon, and the substrates were almost completely etched by the fluorine gas. Micrograph pictures of the microchannels with a scanning electron microscope (SEM) show that the gold layers do not cover the whole
channel surface. The underlying 150 nm thin palladium seed layer is not a sufficient corrosion protection for the substrate due to pinholes in the deposited film. Figure 3-3 compares a gold and a nickel layer in a micrograph of a 100 μm wide and 300 μm deep microchannel. The nickel layer covers with a continuous layer the whole channel wall, while the gold layer stops at the sidewalls at a depth of approximately 150 μm. This effect was detected for all gold layers and all channels widths. Therefore, the palladium seed layer and thus the silicon substrate were exposed to fluorine gas and, consequently, etched. The silicon chips covered with 6 μm thick nickel layers were all etched at the corners and edges between the channel bottoms and walls. This effect is shown in Figure 3-4a with the 100 μm channel at the connection point to a larger channel. The test chips with a nickel thickness of 12 μm withstand the fluorine gas, but some chips were etched at the logo with the small structures of 50 μm, see Figure 3-4b. With a minimum thickness of 16 μm the nickel layer is hermetically tight and prevents a chemical etching of the silicon underneath. All results for the test chips with the different nickel layers are enlisted in Table 3-1. For all layer thicknesses, the current density has no effect on the chemical resistivity and the complete covering of the silicon substrate.

All nickel layers exposed to fluorine show a change of their color from silver to golden-bronze and remain smooth with an average roughness of approximately 30 nm like before the fluorine exposure. Subsequent material analysis with x-ray photoelectron spectroscopy (XPS) reveals that nickel self passivates upon exposure to fluorine and forms NiF₂ salt on the surface that causes the color change. This salt layer provides a sufficient permanent passivation against fluorine gas and hydrogen fluorine for the further use in a direct fluorination microreactor. Figure 3-5 shows the XPS survey spectra of a nickel surface before and after 6 h exposure to 100% fluorine gas. After the exposure the survey spectra the characteristic peak of NiF₂ is visible at 857 eV [27]. This is the expected binding energy of Ni in NiF₂. Hydrogen carbon (C 1s at 285 eV) was used as reference to compare this value with the measured plot in our studies.

Figure 3-3: Comparison of a electroplated (a) nickel and a (b) gold layer in a 100 μm wide and 300 μm deep microchannel. The nickel layer covers completely the channel while the gold layer covers only half of the sidewalls.
Figure 3-4: These pictures show the effect of pinholes in the nickel layer. The silicon underneath is etched as shown in the backside pictures. (a) Up to a layer thickness of 12 μm, the nickel shows pinholes in the edges and corners of the microchannels. (b) The defects of nickel layers between 12 μm and 16 μm are caused by imperfect deposition in the small layer structure of the logo (width 50 μm).

Table 3-1: Chemical resistivity of the electroplated nickel layers (Slotonik 50) after 6 h exposition to 100% fluorine gas. The nickel layers have different layer thicknesses and were electroplated with different current densities (@ 55 °C).

<table>
<thead>
<tr>
<th>layer thickness [μm]</th>
<th>current density [mA/dm²]</th>
<th>chemical resistivity</th>
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<tbody>
<tr>
<td>6</td>
<td>30</td>
<td>etched</td>
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<tr>
<td></td>
<td>40</td>
<td>etched</td>
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<tr>
<td></td>
<td>50</td>
<td>etched</td>
</tr>
<tr>
<td>12</td>
<td>30</td>
<td>good</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>etched (logo)</td>
</tr>
<tr>
<td></td>
<td>50</td>
<td>good</td>
</tr>
<tr>
<td>16</td>
<td>30</td>
<td>good</td>
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<td></td>
<td>40</td>
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<td></td>
<td>50</td>
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</table>
3.3 In-channel fabrication

Electroless plated nickel

Based on the preceding analyses of the electroplated nickel, 16 μm thick electroless plated nickel layers (SurTec®833) were also exposed to 100% fluorine gas for 6 h (1 bar). Again the silicon substrates were not etched by the fluorine gas. This can be attributed to a hermetic sealing of the silicon substrate against fluorine gas attack. The exposure to fluorine again changes the silvery surfaces to a golden-bronze color. However, the surface remains smooth like for the electroplated nickel with an average roughness of approximately 30 nm before and after the fluorine exposure. XPS measurements of the electroless nickel surface obtain the same characteristic binding energy peaks as the electroplated nickel. This is depicted in Figure 3-6 for the electroless nickel and compared with the survey spectra of the electroplated nickel after the exposure to the fluorine gas. Both nickel surfaces shown the same characteristic binding energy peaks and, in particular, the peak of the NiF$_2$ salt at 857 eV.

Figure 3-5: XPS survey spectrum of an electroplated nickel film before and after exposure to 100% fluorine atmosphere for 6 h with 1 bar at room temperature. A typical peak for the nickel fluorite NiF$_2$ (Ni 2p3) occurs at a binding energy of 857 eV.

3.3 In-channel fabrication

In order to show the numerous possibilities of the in-channel electroless plating, several different 2D, 2½D and 3D microfluidic structures are shown in the following. The fabrication technique is similar and differs mainly in the post-formed and stacked microchannel structures. The basic fabrication process is schematically represented in Figure 3-7.
3 Fluorine resistant materials and fabrication methods

First, an etch mask of thermally grown silicon oxide (SiO₂) is deposited on 525 μm thick, double side polished <100> silicon wafers (Figure 3-7a). The SiO₂ thickness depends on the required depth of the subsequent DRIE process which defines the height of the microchannel. As an example, a 150 μm deep channel requires a 2.5 μm SiO₂ layer. A photolithographic step defines the microchannels. After opening the SiO₂ masking layer with reactive ion etching (RIE), the channels are etched with deep reactive ion etching (DRIE), see Figure 3-7b. Afterwards, the oxide mask is removed with hydrofluoric acid (HF). This patterned substrate and the corresponding lid are coated at their front and back side with a vapor-deposited palladium seed layer (150 nm), see Figure 3-7c. A rapid thermal annealing (225 °C, 3 min) in a nitrogen atmosphere forms a palladium silicide interface between palladium and silicon and ensures an excellent adhesion of the seed layer to the silicon substrates [28].

The pretreatment for the electroless plating is a hot electro-degreasing in sodium hydroxide for 10 s [30] and an acid pickling with hydrochloric acid (38% concentration, 50 °C) combined with ultra sonic treatment for 30 s [31]. This is done to remove the surface oxide layer immediately before the electroless plating. The fluidic structure is closed with the lid and an electrolyte solution of electroless nickel is pumped through the fluidic system, see Figure 3-7d. For the 2½D and 3D fluidic system the channel sections are distributed over different substrates, see also Figure 3-8. When the substrates are stacked on top of each other, the channels have an overlap at specific points and thus form a closed fluidic system in three dimensions. The electrolyte solution SurTec®833

![Figure 3-6: Surface XPS spectrum of the electroless plated nickel (SurTec®833) after exposure to fluorine gas. The dashed trace is the survey spectra of the electroplated nickel (Slotonic 50) after the fluorine exposure. Both nickel layer show the characteristic binding energy peak at 857 eV for the NiF₂ salt.](image)
3.3 In-channel fabrication

(SurTec, Germany) is used for the plating process. This is an electroless nickel plating solution with a high concentration of phosphor for high gloss, anticorrosive nickel coatings.

The substrate chips are mounted in a fluidic chip carrier with fluid connectors that is heated in a water bath. The setup for the in-channel electroless plating is displayed in Figure 3-9. A syringe pump (Injectomat 2000, Fresenius, Germany) feeds the continuous liquid flow and the water bath heat is controlled with a hotplate (IKA RCT basic, IKA, Germany). The chip carrier was developed within the working group [32] and was also used for the bubble generation measurements, see subchapter 2.5. The pumping occurs at 92 °C and at Reynolds numbers between $Re = 2$ and $Re = 370$ to achieve a continuous and homogeneous plating of nickel at the inner channel walls. The Reynolds number is calculated with a hydraulic diameter of $d_H = 200 \mu m$ and the density $\rho$ and the dynamic
**Figure 3-8:** This sketch shows a 3D explosion view of the silicon top and bottom substrate with the etched channel sections. The channels have overlaps at specific areas. The substrate surfaces are pressed together to close the 3D fluidic structures. An electrolyte solution is pumped through this system and post-forms the channels with metal.

**Figure 3-9:** The setup for in-channel electroless plating is shown in this figure: (a) complete setup, (b) detailed view of water bath with fluidic chip carrier, and (c) schematic of the setup.
3.3 In-channel fabrication

viscosity $\eta$ depending on the temperature of the liquid electrolyte solution. These values are comparable with water and therewith $\rho = 965$ kg/m$^3$ and $\eta = 314 \times 10^{-6}$ kg/m s. The deposition rate is approximately 6 $\mu$m/h at a pH-value between 4.6 and 5.2. That deposition rate is similar to a conventional deposition with SurTec®833. The deposition rate primarily depends on the temperature and the pH-value of the electrolyte \cite{31} and not on the applied Reynolds numbers in the channel. With a longer reaction time of the electrolyte the pH-value changes. Due to the dependency of the metal plating on the pH-value the residence time and therefore the channel length is limited. The deposited nickel walls post-form the fluid microchannels and additionally bonds the chip substrates together. The final nickel wall thickness of 12 $\mu$m is controlled by the deposition time. During the electroless plating process, hydrogen gas is produced due to the chemical deposition reaction \cite{31, 33}. These gas bubbles have to be removed from the channel which determines the minimum Reynolds number ($Re = 2$) required for a sufficient metal deposition. The formation of the gas bubbles has also to be considered for the design of the microfluidic channels. The channel design has to avoid sticking of the bubbles which can prevent the metal deposition locally or, in worst case, clog the channel. Above the maximum Reynolds number ($Re = 370$) the coating decreases or even stops, possibly due to the reduced residence time of the reactants at the catalytic palladium seed layer. The presented in-channel plating is, in principle, possible with every other metal that can be electroless plated. This was also tested with electroless gold (Aurol 20, AMI Doduco, Germany). However, the seed layer, the pretreatment, and the deposition conditions (temperature, pH-value, and flow rate) have to be adjusted to every electrolyte solution.

At this state the process can be stopped, with internally passivated and nickel-bonded three-dimensional microchannels as a result. As explained, the wafer bonding and microchannel postforming happens in one step. A further continuation provides free-standing nickel microchannels, as explained in the following. After the in-channel nickel plating, the palladium layer which covers the external chip surfaces is partially removed with a Nd-YAG laser \textit{DPL Magic Marker} (ACI Laser, Germany). A 5 $\mu$m thick nickel layer is electroplated with \textit{Slotonik 50} (Schloetter, Germany) on top of the patterned palladium seed layer, see Figure 3-7e and Figure 3-10a. The nickel layer does now serve as an etching mask for the selective KOH etching to release the nickel microchannels from the silicon substrate. The KOH etching (30%, 80 °C) removes the silicon in the patterned area and only the palladium layer between the two substrates and the post-formed metal microchannels will remain as free-standing membrane (Figure 3-7f). Figure 3-10b shows the KOH etching of a 2D microchannel structure after 4 h and Figure 3-10c shows the same structure after 8.5 h etching time with the completely released microchannels. Between the channels the remnants of the palladium seed layer are still visible. These remnants are removed by an ultrasound-aided cleansing bath with abrasive aluminum oxide particles in deionized water (with a concentration of 100 g/l). The aluminum oxide particles (\textit{CT3000 LS SG}, Almatis, Germany) have an approximate surface area to weight ratio of 7 m$^2$/g. After 5 min, the remnants are abraded, as depicted in Figure 3-10d. The
outer channel surface has an average roughness of 5 nm, which is nearly the surface roughness of a silicon substrate. The inner channel surface has an average roughness of 17 nm to 64 nm for a channel wall thickness of 12 μm.

### 3.4 Microfluidic structures

The presented fabrication method provides a great number of design possibilities, from selective nickel coating inside a fluidic structure to 2D, 2½D and 3D microchannels. Besides the microchannel structuring, the in-channel electroless plating achieves a continuous deposition of nickel and enables a strong bond between the substrates in one step, see Figure 3-11a. This bond between the silicon substrates is achieved via the continuous overlapping nickel layer inside the microchannels which is firmly connected to the palladium seed layer on both substrates. The plating method is tolerant even against defects caused by previous fabrications steps, such as cracks or seed layer ablation as shown in Figure 3-11b. The seed layer is a 150 nm thin palladium layer which is bonded to the silicon surface. The bonding can be defective by insufficient cleaning before the vapor deposition or errors in the thermal annealing. As a result, the seed layer can peel off the silicon substrate. In general, these defects are avoided by accurate cleanroom fabrication, however, the robustness of the post-forming process is demonstrated via this non-optimal
3.4 Microfluidic structures

preparation. Furthermore, the electroless plating shows an accurate coating of small microstructures inside the fluidic channels. This is shown in Figure 3-11c for a potassium hydroxide (KOH) etched nozzle with a smallest orifice diameter of 20 μm. The nozzle was contacted with two fluidic channels on top and bottom and the electrolyte solution was pumped through the nozzle for the metal deposition. Furthermore, the nickel deposition enables homogeneous layer thicknesses over long microchannels (up to 5 cm). This is illustrated in Figure 3-11d with a meander channel. This microchannel is in sum (with the part outside the picture) 4 cm long and has a 20 μm thick nickel wall with only 4% thickness derivation.

The homogenous nickel plating to post-form the fluidic structures allows the fabrication of complex 2D microchannel structures either embedded in or released from the surrounding silicon substrate. This is demonstrated with several test structures realized within two-layer silicon stacks. These microchannels are partially released from the surrounding silicon substrate and bridge a gap between the silicon frame up to 8 mm with straight or meander channels, see Figure 3-12. The microchannels have a cross section of 150 μm × 300 μm and a wall thickness of approximately 10 μm. The detailed cross sectional picture of the meander pipe in Figure 3-12c shows the thin nickel wall in

Figure 3-11: This picture shows polished cross sections of (a) a microchannel which is post-formed with a uniform nickel layer of 6 μm and bond the two substrates together. (b) Shows a thicker layer of 12 μm which compensate a debonding of the palladium seed layer. (c) Polished cross section of a KOH etched nozzle. The silicon cracks are caused by the polishing process. (d) Meander microchannel with a homogeneous plated nickel wall of 20 μm ±4%.
comparison to the cross sectional area with a laser cut through the pipe. The fabrication of structures with 2 ½D is shown with a zigzag and a simple mixing channel. Figure 3-13a shows the zigzag channel with a cross section of 150 μm x 300 μm. At these bends, the channels turn into the third dimension from the upper to the lower side of the channel top cover. The simple mixing channel has only three bends, each for one of the three spatial directions, see Figure 3-13b. These structures are called 2 ½D because they are fabricated with only two structured layers. Thus, the length of the connecting channel between the two layers is restricted by the thickness of the layer and the channel cross sectional area. 3D structures can be realized with at least three structured substrate layers. This enables to vary

Figure 3-12: Different silicon test chips with released 2D micropipes (left) and details of the microchannels (right): (a) simple mixing channel, (b) two u-pipes with a straight and meander part, and (c) a long meander pipe bridging a gap of 8 mm. The sectional view shows a the pipe with a removed cover wall.
3.5 Material testing

The in-channel electroless plating allows a continuous deposition of nickel inside a microchannel coated with a seed layer. This nickel layer is able to bond the silicon substrates together and to seal the fluidic structure hermetically tight. Moreover, these features are combined with a good chemical inertness as discussed in the previous subchapter 3.2. The mechanical strength of the realized microchannels was tested with a tensile test for the vertical bond strength, a shear stress for the horizontally bonded structure, and pressure tests for the channel stability. The pressure tests were also used to specify the hermetic tightness. Furthermore, the material was tested for its chemical inertness against fluorine gas.

Figure 3-13: Microfabricated silicon chips with 2½D structured micropipes with a detailed view: (a) zigzag pipe, (b) simple mixing micropipe with three bends.

the length of the connecting channel part between the different levels. Therefore, it is possible to form a fluidic channel which is coiled around itself and, essentially, forms a knot. Such a knot is shown in Figure 3-14 with one microchannel. This channel has a cross section of 300 μm × 300 μm and a wall thickness of 10 μm. For further details to the fabrication of the 2 ½D and 3D microchannels see the master thesis of Neiss [34].
3.5.1 Bond strength

Electroless plated nickel layers can also be used as bond interface between two silicon substrates. The deposited nickel layer has, theoretically, a high tensile strength. However, the influence of the deposition method and the interfacial bond strength between nickel, palladium seed layer, and silicon, hence the bond strength of this total interface is not known. Possible errors are cracks and defects in the nickel layer due to inaccurate plating, a delamination of the nickel layer from the palladium seed layer or a delamination of the palladium layer from the silicon [31]. For first bond strength measurements of the bonding interface of electroless plated nickel, palladium seed layer and the silicon substrate, silicon chips with the dimensions of 1 cm × 1 cm were used. These chips were structured at two opposite outside edges with 8 mm long and 100 μm deep KOH-etched gaps and coated with a palladium seed layer (see chapter 3.3). Two chips were placed on top of each other and were bonded together in the small area of the gaps via electroless plating (SurTec®833, 92 °C). During this process a 10 μm thick layer of nickel was deposited as a conformal coating in the KOH-etched gaps. This is schematically depicted in Figure 3-15a. A detail cross section in Figure 3-15b shows the resulting bond between the chips. The resulting bonding areas with nickel on both sides of the chips were 8 mm long with a thickness of 10 μm. The bonded chips were glued to the grip heads of a tensile testing machine. This testing machine were developed within the working group and presented in [35]. Thereafter, the specimens were stressed to the fracture point. This resulted in an average bond strength of 252 N/mm² ± 61 N/mm² for 30 conducted tests. This is in the range of crystalline silicon from 200 N/mm² to 300 N/mm² while micro structured nickel has a fracture strength of 400 N/mm² to 500 N/mm² [36]. Typically, a fracture of the silicon chip near the bonding area happened before the nickel bond was damaged. The fracture of

Figure 3-14: The pictures show a released 3D micropipe which forms a knot. The cross section of the micropipe is 300 μm × 300μm. (a) Knot with the chip. (b) The detail view of the micropipe knot and (c) a CAD drawing of the knot.
3.5 Material testing

The silicon chip is displayed in Figure 3-15c. This demonstrates a sufficient bond strength and stability of the metal-formed structures.

3.5.2 Bending strength

The stability against elastic strain applied to a 2D u-shaped micropipe was tested with a Dage 4000 (Nordson, USA) bond tester. The u-pipe (cross sectional area: 150 μm × 300 μm; wall thickness 10 μm; lever arm length 2.5 mm) is deflected with the shear head, moved over 500 μm with a maximum force of 1.5 N (±0.2 N) and bends back to its initial position. This is schematically illustrated in Figure 3-16 while the u-pipe is deflected with a syringe needle and after the deflection. The mechanical properties of the micropipes have to be further examined but they show already remarkable opportunities for active microfluidic and MEMS systems.

3.5.3 Pressure test

To determine the pressure stability, 2D U-shaped micropipes were used. These micropipes with the surrounding chip frame are shown in Figure 4b. The micropipes were
connected to a pressure supply at the chip frame. The microfluidic test chip was immersed in water to detect evading air and pressurized for 12 h up to 6 bar. No pressure loss was detected over this time. At the next measurement point of 7 bar, the structure cracked after approximately 1 h. The pressure test was performed with 5 nickel pipes and they showed the same stability up to 6 bar. However, the micropipes show different times of stable operation under 7 bar before the onset of failure. This means, that the micropipes are hermetically tight under high pressure up to 6 bar and that no initial cracks are present that would be widened.

### 3.6 Conclusion

In conclusion, we have presented that electroless and electroplated nickel layers with minimum thickness of 16 μm are a sufficient cover against fluorine gas for micro structured silicon. The nickel layers are chemically resistant against fluorine gas by forming a passivation NiF$_2$ salt layer on the surface. That salt layer was verified by XPS measurements. The chemically resistant nickel was used for a simple microfabrication method to produce freestanding micropipes with a broad range of aspect ratios. This in-channel electroless plating enables a post forming of 2D, 2½D and 3D microfluidic systems with a homogeneous nickel layer. This nickel layer also bonds sufficiently the chip stack together, with a high bond strength, despite the small effective bond area at the matching walls of the silicon substrates. Subsequent selective KOH etching of the silicon substrate allows the release of the metal micropipes to bridge openings of at least 8 mm. These fabricated micropipes with nickel walls of approximately 10 μm thickness are hermetically tight and withstand pressures up to 6 bar. The measured fracture strength of the electroless plated nickel bond is higher than the silicon fracture strength of the substrate of 200-300 N/mm$^2$ and results in a fracture of the silicon near the bond instead of the nickel. Hence, freestanding micropipes are useable for chemical reactors with exothermal reactions and aggressive chemicals.

The post-formed microchannels of the microreactor can be released from the silicon substrate to determine their pressure stability, tightness and strength that are necessary to
withstand the harsh reaction conditions of direct fluorination. Moreover, this technology enables the possibility for further developments of the microreactor. This are for instance 3D mixing micropipes that are directly exposed to a cooling medium. In chapter 6, the enhanced mixing quality of 3D mixing microchannels is presented. Furthermore, the improved heat transfer capability of freestanding metal micropipes is shown.

3.7 References


3.7 References

4 Minireactor

4.1 Introduction

This chapter describes a minireactor system for direct fluorination of organic solvents. Minireactors follow, in principle, the same concept as microreactors, but with larger dimensions in the range of millimeters. This scale of size is small enough to keep the desired features of microfluidics/microreactors, but it is large enough to avoid clogging of the fluidic channels and to facilitate conventional machining of the minireactor system. The conventional fabrication method allows a rapid machining and customization of the minireactor. Therewith, fundamental knowledge of specific direct fluorination reactions, on the resulting reactor design and on the needed chemically resistant materials can be obtained.

Within this study the described minireactor has been realized for the following reasons: (a) Pilot tests for the multiphase flow intended for the microreactor. (b) Test of the nickel passivation and bonding concept. (c) Direct fluorination experiments as proof of concept and for an evaluation of the reaction conditions.

The multiphase fluidic system of the minireactor is characterized for a slug flow regime and the resulting interfacial area at different volume flow rates. That interfacial area is used as contact zone between the liquid substrate and the fluorine gas. Slug flow enhances mixing, heat transfer and provides large interfacial areas for the fast and heat extensive fluorine reaction. The reaction heat generated during the direct fluorination of toluene and ethylene carbonate (EC) are analyzed to find the reaction speed for a complete reaction conversion in the reactor. Furthermore, the direct fluorination of EC in the fabricated minireactor is described in detail, including a discussion of the results of the chemical reaction.

While fabricated with conventional machining the channels of the minireactor were encapsulated with the in-channel electroless plating technique described in chapter 3. This plating method provides a gas-tight and fluorine resistant nickel layer inside the channel. With a first implementation in the minireactor, this technique was tested for further application in the microreactor. Also, the application of in-channel plating and stack bonding was demonstrated for copper as an alternative substrate material. Furthermore, it was possible to test different liquid solvents, substrates and types of reaction control with the minireactor. During these tests, the temperature of direct fluorination was monitored to obtain first information of the reaction heat and the reaction time. This information allows to design the active cooling and the residence time that is needed in the minireactor and, thereafter, in the microreactor.

The most successful chemical tests of the minireactor were done with a reaction of EC...
and fluorine gas (F₂) to produce fluorinated EC (F₁EC). This product is suitable for use as additive solvent in lithium ion accumulators [1]. It features benefits like excellent oxidation durability, wide liquidus range and non-flammability that are interesting for safety issues in accumulators [1, 2]. It turns out that the minireactor facilitates the direct fluorination in continuous flow of 30 ml/h to 150 ml/h liquid flow rate with a gas flow of 400 ml/h at room temperature and with a high yield. Moreover, the fluorine gas concentration can be set between 45% and 88% with a complete reaction conversion.

4.2 Minireactor - design and fabrication

4.2.1 Design

The minireactor system consists of unit components distributed on a stack of structured nickel-plated copper plates with a footprint of 10 cm × 10 cm. These components are tubing connectors for the fluidic inlet and outlet of the reactor, a T-junction nozzle for the gas bubble injection, a fluid minichannel for the chemical reaction, temperature sensors located at the chemical reaction minichannel and an active minichannel heat sink.

The unit operation of gas injection is a T-junction made of a gas channel and the reaction channel. Figure 4-1 shows a sketch of the two channels that merge in a right angle.

![Figure 4-1](image)

*Figure 4-1*: This schematic sketch shows the T-junction for the slug generation. The slug length can be adjusted by the gas and liquid volume flow rate. The chemical reaction occurs at the interface and depends on the diffusion rate of EC and fluorinated EC. The mixing of the liquid phase is enhanced due to the slug flow.

The discontinuous gas flow of the gas channel penetrates into the continuous liquid flow in the reaction channel. Therefore a bubble grows inside the reaction channel until it fills almost the entire reaction channel and is moved downstream the continuous flow. The bubble is disconnected when the interfacial neck at the gas channel inlet is cut off by the continuous flow. Afterwards, a new bubble begins to grow in the reaction channel. Garstecki et al. [3] propose a break-up mechanism caused by the pressure difference.
upstream and downstream the growing bubble. With this model, the injected bubble length can be determined by the volume flow rates. This setup can generate monodisperse bubble slugs over a broad range of gas and liquid flow rates. With the moment of the bubble generation, the reaction of EC and fluorine gas starts at the interface and is continued while the slug flows in the reaction channel. Direct fluorination depends on the diffusion of EC and fluorinated EC near the interface for the reaction. This diffusion process is improved by an increased interfacial area and the enhanced mixing behavior between two slugs [4]. Furthermore, this mixing improves also the heat flux for the fluid cooling. This heat flux is dissipated with an active heat sink of parallel minichannels perpendicular to the reaction minichannel.

The schematic drawing in Figure 4-2 illustrates all unit components in top view. The liquid enters the reaction minichannel of 1 mm × 1 mm cross section via a tube connector in the first plate and a boring of 1 mm diameter in the second plate. Hence, the gas is injected via a T-junction that is easy to fabricate and well described in literature [3]. The liquid is transported over a distance of 115 mm with three bends through the reaction channel to the drilled gas nozzle. The distance between all meandering loops of minichannels is 3 mm. After the channel section with the gas nozzle, the distance between the first loops is 9 mm, because most of the reaction and therefore the generated heat occur.
in these first centimeters of the reaction minichannel. Further downstream of the reaction minichannel follow ten more bends with a loop distance of again 3 mm. This results in a total channel length of 417 mm with multiphase flow between the gas nozzle and the minichannel outlet. Temperature sensors are located at the backside of the second plate, 1 mm under the reaction minichannel at 1 cm, 2 cm, 4 cm, 30 cm, and 53 cm downstream of the nozzle to monitor the temperature distribution over the channel length. The active heat sink in the third plate covers the complete reaction minichannel. It is an array of 14 parallel, 37 mm long minichannels with cross sections of 2 mm × 2 mm. All channels are divided by 2 mm thick walls and run nearly perpendicular to the long parts of the meander loops of the reaction minichannel. The mismatch of about 9° results from design considerations concerning the screw joints to combine the structured plates. The cooling flow is mainly in flow direction of the reaction minichannel. Hence, the cooling ratio is most efficient near the gas injection where most of the heat is generated. The material thickness between the reaction minichannel and the cooling minichannels is 1 mm. Inlet and outlet chambers for the cooling array are 10 mm wide and narrow down to 2 mm at the last cooling minichannel. This follows the design rules of Commenge et al. [5] for a homogeneous flow distribution in the minichannel array. The inlet and outlet hose connectors for the cooling liquid are in the fourth plate which also covers the cooling system. Figure 4-3 shows the different layers of the machined minireactor.

**Figure 4-3:** The minireactor is subdivided into different layers. Layer 1 is for the connecting tubes to the reaction minichannel that is in layer 2. These minichannels are covered with the backside of layer 3. On the topside of this layer is the active heat sink with its parallel minichannels. The heat sink is covered and connected with layer 4 to the cooling liquid circuit.
4.2.2 Fabrication

The minireactor, as shown in Figure 4-3, is a multilayer construction with four structured copper plates. The copper is machined with conventional milling. After an electro-coating of the structured plates with chemically resistant nickel, the plates are mounted together with screw joints to cover the fluidic structures in layer 2, 3 and to fix the hose connectors in layer 1, 4.

In detail, the fabrication of the minireactor was realized as follows: The fluidic channels for the reaction channel and the cooling system were milled into 4 mm thick copper plates. For a gas-tight sealing of the reaction channel, two round pinch seals were also machined to the reaction channel layer. They were 50 μm thick and 100 μm wide. After milling, all structured copper plates were electroplated with 20 μm thick high gloss nickel using Slotonik 50 (Schloetter, Germany) to form a permanent passivation against fluorine gas and hydrogen fluoride [6, 7]. At the back side of the reaction layer five temperature sensors (Type T, Labfacility, UK) were placed into 2 mm deep, milled connecting channels. At the nearest wall to the reaction minichannel, they were fixed with conductive silver adhesive. The reaction minichannel was connected to the fluidic tubes via the boring in the first layer (1 cm thick nickel-plated copper) and covered with the backside of active heat sink layer such that the cooling minichannels were positioned above the reaction minichannel. Due to the pressure applied by ten screws around the pinch seal, the pinch seals were pressed together and the reaction minichannel was closed. Afterwards, the reaction minichannel was additionally sealed by an in-channel electroless plating process. The pretreatment for the electroless plating was a hot electro-degrasing in sodium hydroxide for 30 s (0.3% concentration, 70 °C) and an acid pickling with hydrochloric acid (38% concentration, 25 °C) for 1 min to remove the surface oxide layer. The electrolyte solution SurTec®833 (SurTec, Germany) was pumped through minichannel and nozzle with a flow rate of 10 ml/h, each. The pumping occurred at 92 °C and a pH value between 4.6 and 5.2 achieving a continuous and homogeneous plating of nickel with deposition rates of approximately 6 μm/h. The final nickel wall thickness of 12 μm was controlled by the deposition time (2 h). Due to the combination of the pinch seal and the in-channel nickel plating the reaction minichannel was sealed gas-tight. The channels of the heat sink were covered with a 10 mm thick nickel-plated copper, including the fluid connectors for the cooling (see Figure 4-3, layer 4). This layer was mounted with four screws on the O-ring seal that closes sufficiently the cooling system.

4.3 Fluidic test

The hydrodynamic effects of the multiphase flow were analyzed to determine effects on the chemical reaction between fluorine gas and liquid EC solvent. Due to a recirculating liquid flow between the bubbles, the slug flow regime enhances significantly the mixing and the reaction performance of the reactor [8, 9]. Moreover, slug flow intensifies the heat
4.3 Fluidic test

transfer of microchannel heat sinks [9]. However, the mixing and heat conduction capability is not determined in detail for the presented minireactor. Since mixing and cooling is sufficient for our system parameters, no difference of heat transfer or mixing between different slug flows can be measured. In this work, we analyze the slug flow for its regime limits and the gas slug length. With the slug length, the resulting gas-liquid interfacial area relative to the liquid volume flow in the reaction minichannel can be determined.

4.3.1 Test setup

For an optical observation, the reaction minichannel was covered with an optically transparent plexiglas (PMMA) cover and a flexible polyurethane (PU) gasket. The gas and liquid flow were fed with syringe pumps (Injectomat 2000, Fresenius, Germany). To detect the front and backside of a flowing gas slug, two differently colored light-emitting diodes were placed in and against the flow direction of the channel section with the gas nozzle (green and blue, 5 W Luxeon V Star, Lumileds, USA). Therewith, the spherical front side of a gas slug reflects the green and the spherical back side reflects the blue light, see Figure 4-4a. Pictures of the channel section with the nozzle were made with a digital camera (EOS 500D, Canon, Japan) at different gas and liquid volume flow rates. The pictures were analyzed for the gas slug length, see Figure 4-4b.

The gas-liquid interface $O_{\text{slug}}$ of one slug was calculated by the spherical surfaces of the front and back of the slug in $O_{\text{sphere}}$ and the cylindrical surface $O_{\text{cylinder}}$ between front and back. As the slugs are transported slightly faster than the liquid, the liquid flows around the whole slug interface [10, 11]. The equation is

\[
O_{\text{slug}} = O_{\text{sphere}} + O_{\text{cylinder}}
\]

\[
O_{\text{slug}} = 4\pi \cdot r^2 + 2\pi \cdot r \cdot l
\]  

(4.1)

where $r$ is half of the channel width $w$ of 1 mm and $l$ is the length of the cylindrical part of the slug length $L$ ($l = L - 2r$). This is schematically shown in Figure 4-4c. The typical bullet-shaped form of a slug flowing in a microchannel [12] and the ellipsoidal interfacial shape due to the contact angle of 15° (between 2-propanol and nickel) is simplified to two spherical shapes. It is also to mention that the cylindrical form of the slug body is a simplified assumption of the realistic cross-section. This would be a shape between a cylindrical and quadratic form due to the capillary corner flow of the liquid [13]. The real shape is difficult to determine in measurements and the cylindrical assumption is sufficient to compare the slug interfaces of this minireactor system. With the interface of one slug, we can calculate the overall interfacial area $O_s$ relative to the liquid flow in the minireactor

\[
O_s = \frac{f \cdot O_{\text{slug}}}{V_l}
\]  

(4.2)
with the measured slug generating frequency \( f \) and the liquid volume flow rate \( \dot{V}_1 \). Since fluorine has a low solubility in commonly used organic solvents, the reaction proceeds at the gas-liquid interface. Therefore, the interfacial area determines the fluorination process. This implies that the control of the interfacial area allows to control the delicate direct fluorination process.

### 4.3.2 Fluidic measurements

To assure non-hazardous experimental conditions 2-propanol was used as continuous phase and nitrogen gas as dispersed phase in all fluidic tests, instead of EC and fluorine gas. These substances show comparable fluidic behavior for a two-phase flow system at room temperature with maximum 5% difference in the measured bubble length. This was tested in measurements that compare 2-propanol and EC for bubble generation in the reaction minichannel for liquid flow rates of 50 ml/h, 100 ml/h, 200 ml/h, and 400 ml/h. For each liquid flow rate the slug length was measured with a nitrogen gas flow rate of 50 ml/h, 100 ml/h, 200 ml/h, and 400 ml/h, respectively.

The measurements to determine the slug lengths of nitrogen gas in 2-propanol were

![Diagram](image-url)
done with different constant liquid flow rates with a variation of the gas flow rate. The measured slug lengths are plotted in Figure 4-5. The lengthening of the gas slugs at the end of the minichannel due to the pressure loss is neglected. The measured pressure loss is in worst case 50 mbar and the maximum lengthening is 4% of the original length. For a theoretical background of pressure loss for multiphase slug flow in micro-/minichannels see [32]. Furthermore, first observations of the reaction had shown that most of the reaction occurs in the first centimeters of the reaction minichannel (total length: 41.7 cm).

The different liquid flow rates were measured between 5 ml/h and 400 ml/h gas flow rate. For the presented minireactor system, it is important to stay in the flow regime of slug flow between the annular flow regime above and the bubbly regime below [15]. Bubbly flow occurs when the gas flow that penetrates into the liquid channel is not fast enough to grow to the size of the entire channel before it is sheared off by the liquid flow. Therefore, bubbly flow describes bubbles smaller than the reaction minichannel. Annular flow describes a core flow of the gas, surrounded by the flowing liquid. This means that the shear force and the pressure difference between gas and liquid are not high enough to break-up or squeeze the gas flow. The mechanism of the regime change is not theoretically analyzed till present but the observed regime limits of Cubaud et al. [16] correspond to the presented regime limits of the reaction minichannel. The slug flow regime limits of the 5 ml/h liquid flow rate is above 100 ml/h gas flow rate. For the 10 ml/h liquid flow rate the regime limit is above 300 ml/h gas flow rate. The 25 ml/h liquid flow rate starts with slug flow from 50 ml/h gas flow and the slug flow regime of the liquid flows of 300 ml/h.

**Figure 4-5:** This graph shows the gas slug length for a variation of the gas flow rate between 5 ml/h and 400 ml/h and a fixed liquid flow rate. Eight different fixed liquid flow rates are shown between 5 ml/h and 400 ml/h. The solid lines serve as visual guides.
and 400 ml/h starts at 25 ml/h gas flow. For the liquid flow rates of 50 ml/h, 100 ml/h, and 200 ml/h no regime limits for slug flow were detected. In general, except for the kinks at a gas flow rate of 25 ml/h, the gas slug lengths increase linearly for increasing gas flow. Furthermore, the linear gradient for the slug length decreases with increasing liquid flow rates. This corresponds with the theoretical model and the measurements for bubble generation in microchannel T-junctions of Garstecki et al. [20]. The kinks of the liquid flow rates 5 ml/h, 10 ml/h, and 25 ml/h at the gas flow rate of 25 ml/h were not further analyzed. They are assumed to be caused by measurement failures or a defect of the measurement setup for gas flow rates up to 25 ml/h.

The interfacial area per liquid volume flow \( O_\text{s} \) is calculated with the interfacial slug area and the slug generating frequency. Figure 4-6a shows \( O_\text{s} \) for different liquid flow rates and a gas flow rate variation between 5 ml/h and 400 ml/h. The values of \( O_\text{s} \) increase with a power law model for increasing gas flow (\( f(x) = ax^2 \)). Furthermore, the increase of the interfacial area gets smaller with increasing liquid flow rates. Liquid flow rates from 100 ml/h to 400 ml/h are illustrated in detail in Figure 4-6b. The determined interfacial area demonstrates that an identical interfacial area per liquid flow can be generated with different gas-to-liquid flow rates due to the changing slug lengths.

### 4.4 Temperature measurements

Direct fluorination is a very fast mass transfer limited and exothermic reaction. Reaction tests with temperature measurements were performed to assure that this reaction proceeds only inside the minireactor with the active heat sink. Two different tests without active cooling were done to get a first impression how fast the fluorine reacts within the minireactor. One reaction was a direct fluorination of toluene and the other was a direct fluorination of EC. These reactions were tested with a different temperature measurement setup because they were done at different iteration steps of the minireactor system. The temperature sensors (Type T, Labfacility, UK) were measured with a data logger (LE-LOG_1623, LeTe, Germany) and analyzed with the data logger software. The temperature measurement of the direct fluorination of toluene was only possible from outside the minireactor and required an adiabatic measurement. This was not necessary for the direct fluorination of EC because of temperature sensors were located at the reaction minichannel. Therewith, the temperature course was monitored along the minichannel.

#### 4.4.1 Direct fluorination of toluene

For the direct fluorination temperature measurement of toluene an adiabatic setup was used. The minireactor was placed inside a thermally insulating polystyrene box and the temperatures were measured at the toluene inlet, the product outlet, at the reactor copper body, inside the box, and, in addition, in the ambient. The reaction was performed for 40 min without active cooling, because otherwise no temperature differences would have
been detected. Toluene was fed with 90 ml/h and a F₂-N₂ mixture with 86% F₂ in N₂ was injected with 400 ml/h. This resulted in a total volume flow after the nozzle of 490 ml/h and hence a residence time of 3.1 s. The reaction was monitored over 40 min and the temperature increased continuously for the fluid temperatures, the reactor temperature.

**Figure 4-6:** (a) This graph shows the total interfacial area $O_s$ related to the liquid flow rate $\dot{V}_l$. The solid lines serve as visual guides. (b) The detail graph shows $O_s$ to a maximum of $1 \times 10^6$ $m^2/m^3$ to illustrate the liquid flows from 100 ml/h to 400 ml/h.
and the temperature in the polystyrene box as shown in Figure 4-7. The temperature of product outlet and the reactor body increased after 40 min reaction from 23.8 °C up to 27.8 °C. In the same time, the temperature inside the box was raising from 24.3 °C to 26.5 °C, whereas the ambient temperature remained around 24 °C. With this simple setup approximately 87% ±5.2% of the theoretically possible produced energy was detected. This means, that the reaction occurred completely inside the minireactor and during the residence time of 3.1 s. This was verified by subsequent tests of the liquid product with potassium iodide. With this test, no fluorine was detected in the product outside the minireactor.

![Figure 4-7: This graph shows the temperature measurements during a direct fluorination reaction with toluene without active cooling inside a simple calorimetric setup. The flow rates were 400 ml/h for gas (F₂/N₂ with F₂ = 86%) and 90 ml/h for toluene.](image)

### 4.4.2 Direct fluorination of EC

The temperature measurements of a direct fluorination reaction with EC were performed along the reaction minichannel. Temperature sensors were placed at five different channel sections downstream the nozzle (1 cm, 2 cm, 4 cm, 30 cm, and 53 cm). The minireactor was fed with volume flow rates of the liquid substrate (59% EC solved in Acetonitril) of 40 ml/h and 360 ml/h for the gas (F₂/N₂ with F₂ = 33%). Without an active cooling the temperatures were measured and displayed in Figure 4-8. The measurement showed higher temperatures within the first 4 cm compared to the following channel length. At 1 cm downstream the nozzle, the temperature was at 26.6 °C and decreased down to 26.4 °C at 4 cm. For the following channel, until 53 cm downstream
4.5 Direct fluorination of ethylene carbonate

The tests for the direct fluorination in the minireactor system were performed by our project partners at the Laboratory of Molecular and Coordination Chemistry, University of Freiburg. They are described in detail to show the chemical application and characterize the performance of the minireactor system.

4.5.1 Experimental setup

Pure fluorine (99.99%, Solvay Fluor, Belgium) was used as fluorine source for the direct fluorination experiments in the minireactor and was diluted with nitrogen (99.999%) to the desired ratio. Commercially available EC (99%, Alfa Aesar, USA) was used as an educt and \( \text{F}_1 \text{EC} \) as a solvent (Solvay Fluor, Belgium). The piping of the setup was constructed with Monel or perfluoroalkoxy (PFA) tubes and Monel-connectors (Swagelok, USA). The
fluorine inlet pressure was measured with a pressure sensor (*Baratron*, MKS, USA). The flow of the gases were controlled by two mass flow meters (*M330*, MKS, USA) and mixed in a T-shaped Monel connector. The fluorine delivery system was carefully leak-tested and slowly passivated using an increasing fluorine concentration up to 50% fluorine. Before the first experiment was performed, the minireactor was cleaned with acetone, dried with nitrogen gas and passivated by a nitrogen gas flow with increasing fluorine concentration up to 50%.

Figure 4-9 shows the whole experimental setup in a diagram. The microreactor was cooled with 2-propanol with a cooling flow of 2.5 l/min and 22 °C was fed with a cryostat (*RL6CS*, Lauda, Germany). The temperatures in the reaction minichannel were detected with thermo elements (Type T, Labfacility, UK) and monitored by a data logger (*LE-LOG_1623*, LeTe, Germany) and a PC. During all experiments, no heat distribution was observed. That proves the very efficient cooling with the active heat sink of the minireactor.

**Figure 4-9:** Diagram of the experimental setup for the direct fluorination of EC in the minireactor.

The minireactor was fed with the mixed fluorine and nitrogen gas flow and a liquid flow. This liquid flow was fed by a peristaltic pump (*Masterflex L/T*, Cole-Parmer, USA) with PFA tubes. EC and F1EC were mixed outside the reactor with inert conditions and filled into the pump. After starting the nitrogen flow into the minireactor, the pump started on a low flow of 30 ml/h. When stable gas slugs were observed at the minireactor outlet, the
liquid flow was carefully increased to the desired level between 30 ml/h and 150 ml/h. When the system was running stable, the fluorine flow was started and turned off after the desired reaction time. The gas and liquid flow ratios are within the slug flow regime to guarantee optimal mixing and heat transfer, see chapter 3. A gas-liquid separation vessel was used at the minireactor outlet to separate nitrogen, parts of hydrogen fluoride and possibly the rest of fluorine from the liquid. All waste gases were pumped through a soda lime filled PFA vessel to deactivate all toxic components. The liquid product was fed back to the pump for a recirculation of the product through the minireactor to gain higher concentrations of fluorinated EC. After the reaction time the liquid flow was switched off 5 min after the fluorine flow was turned off. The nitrogen flow was switched off after further 20 min of purging the PFA vessel and the reactor.

The complete experiment setup for the fluorination of EC in the minireactor is shown in Figure 4-10. The liquid product was transferred into a different vessel to scrub the hydrogen fluoride with excess sodium fluoride (3 g per 3 g EC) and Acetonitrile (4 ml per 3 g EC). Para-fluoro-toluene was used as internal standard (typically 1 g per 3 g EC) and the mixture was stirred for 2 min. After filtration, a nuclear magnetic resonance (NMR) spectroscopy sample of the filtrate was prepared. For the analysis of the samples an Advance II+ 400 (Bruker, Germany) with a 5 mm broadband fluorine observation (BBFO) head was used. The settings for the $^{19}$F-NMR spectra at 377 MHz were a spectral width of 41,667 Hz, an acquisition time of 3.15 s and a relaxation delay of 30 s. The size of the

![Figure 4-10: This picture shows the experiment setup for the cyclically direct fluorination of EC. The setup consists of the minireactor, the cyclic peristaltic pump, the gas mass flow sensors and the gas separator. The soda lime, to clean the separated gas, is not shown in the picture.](image-url)
spectra was 262,144 data points. For the $^1$H-NMR spectra at 400 MHz a spectral width of 6410 Hz, an acquisition time of 5.11 s with a delay of 30 s was used. The spectral size was 65,536 data points. The error on these measurements were around 1%.

4.5.2 Fluorination studies

The fluorination of EC was chosen as model reaction because of its simple symmetric molecular structure with just four hydrogen atoms, see Figure 4-11. Moreover, F$_1$EC [4-fluoro-1,3-dioxolan-2-one (A)] is used as a solvent additive in lithium batteries and produced on a few tons per annum scale, which would be in the desired range for commercial microreactor production [1].

The fluorination of EC results in the fluorinated F$_1$EC that is 4-fluoro-1,3-dioxolan-2-one (A) or in three difluorinated compounds of F$_2$EC: cis-4,5-difluoro-1,3-dioxolan-2-one (B), trans-4,5-difluoro-1,3-dioxolan-2-one (C) and 4,4-difluoro-1,3-dioxolan-2-one (D).

Pure EC is a solid with a melting point of 37 °C, F$_1$EC was used as a solvent [17]. This leads to lower selectivity, due to the possible formation of difluorinated EC (F$_2$EC), but allows for a straightforward separation of the final product. F$_2$EC occurs in three different isomers [cis-4,5-difluoro-1,3-dioxolan-2-one (B), trans-4,5-difluoro-1,3- dioxolan-2-one (C), and 4,4-difluoro-1,3-dioxolan-2-one (D)]. Previous experiments reveal that 4 wt% to 20 wt% of F$_1$EC are sufficient to dissolve EC and enable a reaction in the liquid state at 30-37 °C. This is necessary, because in our setup, it is impossible to heat the tubing to prevent recrystallization of the dissolved EC with only 20 wt% percent F$_1$EC. Therefore, 30 wt% (26 mol%) F$_1$EC were used for all experiments. The conversion $C$, the F$_1$EC yield $Y$ and the selectivity $S$ were determined with:

$$C = \frac{100}{n_{EC}} \cdot \left( n_{F_1EC} + \Sigma n_{F_2EC} \right),$$  

(4.3)

$$Y = \frac{100}{n_{EC}} \cdot n_{F_1EC},$$  

(4.4)

$$S = \frac{100}{n_{F_1EC} + \Sigma n_{F_2EC}} \cdot n_{F_1EC},$$  

(4.5)
where \( n \) represents the molar amount of EC, F\(_1\)EC, and F\(_2\)EC, respectively. The goal of the direct fluorination of EC was to achieve a high yield of F\(_1\)EC. Therefore, a high conversion and a low generation of difluorinated F\(_2\)EC was necessary. To reach the desired high conversion, the fluorine has to react completely with the EC without causing fragmentation, which requires a good mixing as well as a careful temperature control.

Figure 4-12 shows a typical \(^{19}\)F-NMR spectrum of the reaction mixture. In this spectrum, only very small amounts of side products besides F\(_1\)EC and the expected F\(_2\)EC-isomers were observed. They were below < 2% with respect to F\(_1\)EC, even with harsh reaction conditions, for example during the fluorination with 88% fluorine.

Table 4-1 shows a representative set of fluorination experiments. The yields and selectivities are slightly lowered by a higher F\(_1\)EC solvent content. Variation of the reaction conditions led only to small changes in the reaction results, which indicates that this system has to be extremely stable. Especially the fact that a high fluorine content (up to 88%) during the reaction does not lower the yield shows an excellent heat control. Furthermore, the variation of the interfacial areas due to different gas and liquid flows show no effect on the reaction. In Table 4-1 the results of three more classical approaches are also shown. All three are one-reactor batch reactions, in which diluted fluorine is bubbled through pure EC or EC diluted with F\(_1\)EC [18, 19]. To compare these values, it is necessary to note that the results obtained with the minireactor are non-isolated yields and that the other experiments were on an at least few hundred gram scale. Comparing the results, the yields are comparable with the results of Woo et al. [18] and Böse et al. [17], which both are patented as optimized processes. The approach of Kobajashi et al. [19] was a relatively simple lab approach using a PFA vessel. Compared to these examples, the minireactor process is clearly superior. The conversion of valuable fluorine with a fluorine use up to 95%, while using a significant higher fluorine concentration at the same time is the main advantage.

Figure 4-12: This picture shows a \(^{19}\)F-NMR spectrum illustrating the observed products. The reaction conditions were: 0.5 eq. F\(_2\), 400 ml/h gas flow, 45.5% F\(_2\), 30 ml/h EC/F\(_1\)EC, T = 22 °C. para-fluortoluene was added as an internal standard.
Table 4-1: Results fluorination experiments using the minireactor. All experiments were carried out with a mixture of 30%wt of F<sub>1</sub>EC in EC. The liquid flow was 150 ml/h for all experiments except no. 7. In this experiment a liquid flow of 30 ml/h was used. No. a, b and, c are literature values of a: Woo et al. [18], b: Kobajashi et al.[19], c: Böse et al.[17].

<table>
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<tr>
<th>No.</th>
<th>n(F&lt;sub&gt;2&lt;/sub&gt;)/n(EC)</th>
<th>F&lt;sub&gt;2&lt;/sub&gt; conc.</th>
<th>T</th>
<th>F&lt;sub&gt;1&lt;/sub&gt;EC</th>
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<td>23</td>
<td>78</td>
<td>83</td>
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</tr>
<tr>
<td>a</td>
<td>1.2</td>
<td>30</td>
<td>45-50</td>
<td>75</td>
<td>57</td>
<td>93</td>
<td>59</td>
</tr>
<tr>
<td>b</td>
<td>1.8</td>
<td>30</td>
<td>50</td>
<td>70</td>
<td>38</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>c</td>
<td>0.89</td>
<td>5</td>
<td>30-35</td>
<td>56</td>
<td>63</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
4.6 Conclusion

In this chapter a new multiphase minireactor system for direct fluorination of organic solvents has been presented. The minireactor includes a slug generation, a reaction channel with an active heat sink, temperature sensors along the reaction minichannel and a chemically (F₂, HF) resistant nickel coating of all wetted surfaces. The generated slugs were analyzed for their slug length, the resulting interfacial area per liquid volume flow, and frequency. With increasing liquid flow rate or decreasing gas flow rates the gas slug length decreases. That enables to determine the interfacial area with different gas-liquid ratios for the chemical reaction in the minireactor. The active heat sink facilitates a sufficient cooling of the reaction to a temperature of 22 °C for all reaction conditions. Measurements with the temperature sensors have shown that the temperatures in the reaction minichannel remain at the adjusted temperature of the cooling system. Temperature measurements of a toluene and EC fluorination without active cooling have demonstrated that the reaction occurs completely inside the reactor within the first centimeters of the reaction minichannel. This means that only 36 ms reaction time is required for the EC fluorination. All these reactions were performed in one minireactor for at least 100 h process time in sum and no corrosion of the nickel surface was detected. This proves the aptitude of the in-channel electroless nickel plating for the further use in the microreactor. Direct fluorination was possible with fluorine concentrations of 45% and up to 88%. The reaction products were analyzed with NMR spectroscopy and show a fluorine conversion of 83-95% with a F₁EC yield of 60-79% even though the experiments were only done in small amounts and the results are non-isolated yields. These reaction results and the possibility to control the temperature with excellent mixing conditions shows the main advantages of the minireactor system.

4.7 References


5 Microreactor

5.1 Introduction

Direct fluorination of liquid solvents proceeds mainly at the gas-liquid interface that therefore determines the reaction performance of a two-phase microreactor. Furthermore, direct fluorination is a very fast reaction with an excessive heat generation. For example, fluorination of toluene has a reaction heat of $\Delta H = 470$ kJ/mol. These facts determine the microreactor requirements for direct fluorination. The rate of heat and mass transfer in multiphase microreactors is defined by the specific interfacial area and the mixing performance. The interfacial area can be adjusted with the monodisperse generated bubble size. Mixing and optimized heat transfer for cooling the reaction to room temperature are enhanced by 2D meander channels. Heat conducted out of the microchannel is absorbed by an active microstructured heat sink. The silicon-based microreactor is covered with a chemically resistant nickel layer to withstand the highly corrosive direct fluorination environment. This nickel layer seals the reactor gas-tight and, furthermore, bonds the individual reactor layers together.

This chapter describes the design, fabrication and first tests of the silicon-based microreactor for direct fluorination of liquid solvents. For the generation of monodisperse bubbles a rectangular KOH-etched nozzle was used, as described in chapter 2. The 2D meander channel for enhanced mixing and heat transfer was designed according to previous activities within the working group [1] and was analyzed by computational fluidic dynamics (CFD) simulations. The active heat sink was designed as parallel cooling channels flowing crosswise to the reaction channel. Additionally, the heat sink was calculated for a worst case scenario to determine the minimum required cooling performance. This calculation was confirmed by a heat transfer test setup. The microreactor structures were sealed with an in-channel electroless nickel plating process, see chapter 3. The nickel layer was tested as a corrosion-resistant cover for the silicon substrate against fluorine gas. This facilitates, in principle, the first direct fluorination reactions of ethylene carbonate (EC) with the microreactor as the next step of the project and is currently in process. This is comparable to the performed reaction in the minireactor system, see chapter 4.1.
5.2 Design

The microreactor consists of different unit operations distributed over different silicon layers of a chip stack and integrated into the reactor platform. The silicon layers with the different unit operations are displayed in Figure 5-1. The unit operations are the bubble generation with the nozzle layer 1, mixing and heat dissipation in the reaction microchannel layer 2, the active heat sink layer 3 and the fluidic connection to the reactor platform.

![Figure 5-1: Schematic sketch of the three silicon layers of the microreactor. Layer 1 with the gas nozzle and the liquid connection to the platform, layer 2 with the reaction microchannel, and layer 3 with the active heat sink.]

5.2.1 Nozzle

The nozzle in the silicon layer 1 for monodisperse bubble generation is a rectangular 20 μm × 80 μm KOH orifice, according to the results in chapter 2. The nozzle has an inverted and truncated pyramid-shaped form achieved via KOH etching in <100> silicon wafers. This form enables an uniform nickel deposition with electroless plating. Furthermore, the rectangular nozzle opening with the small side in flow direction generates the smallest bubbles at high gas flow rates. The bubble diameters are, for instance, 224 μm for a gas flow rate of 55 ml/h and a liquid flow rate of 97 ml/h. An identical nozzle size with the wide side in flow direction shows for the same flow rates bubble sizes of 226 μm. A quadratic nozzle with 40 μm × 40 μm (which is the same cross sectional area) has shown slightly larger bubble diameters of 230 μm.

The 20 μm × 80 μm nozzle is etched through the nozzle silicon layer (layer 1) and connected to the reaction microchannel in the next silicon layer (layer 2) with an orifice of 60 μm width and 120 μm length. The short side of the nozzle is in flow direction of the
liquid and positioned in the middle of one channel sidewall, see the sketch in Figure 5-2. The nozzle has a height of 525 μm, which is the thickness of the silicon substrate. The KOH nozzle has sloped sidewalls of 54.74° with respect to the wafer surface. Hence, the nozzle area size increases to 802 μm × 862 μm at the nozzle inlet. After a 20 μm thick nickel layer coating of the nozzle, the nozzle orifice is finally 20 μm × 80 μm.

![Diagram](attachment:figure5-2.png)

**Figure 5-2:** This figure shows the KOH nozzle (a) in a three dimensional sketch with the liquid channel bottom and (b) in a top view. The top view shows the etched silicon nozzle size (60 μm × 120 μm) and the nozzle size with the 20 μm thick nickel layer (20 μm × 80 μm).

### 5.2.2 Reaction microchannel

The reaction microchannel in the silicon *layer 2* of the microreactor (see Figure 5-1) has to perform different tasks. The microchannel has to perform a sufficient mixing and an effective heat conduction out of the liquid due to the fast and highly exothermic reaction. Direct fluorination is a reaction at the gas-liquid interface of the fluorine gas bubbles in the microchannel. Hence, the reaction rate is determined by the convection of the liquid around the bubble interface. In a straight microchannel, the bubble (which is smaller than the channel) would flow nearly at the same speed as the surrounding liquid. This means that there is only limited convection around the bubble. Mixing of the liquid flow and therefore the bubbles can be realized with 2D meander microchannels. A meander microchannel with a laminar flow regime generates a pair of counter rotating double
vortices in both halves of the microchannel that do not intermix [2, 3], see Figure 5-3. In curved channels, this typical vortex pair is known as Dean vortex. This affects the track of the bubble in the liquid flow and induces a convection around the bubble. Therefore, it is of interest, how the bubble flows in the microchannel relatively to the main flow and the two liquid vortices. This behavior of a bubble track smaller than the channel is hitherto not reported in the literature for micro dimensions. Although 3D microstructures show better mixing quality, 2D structures were used for the microreactor. The reason is, that the 2D microchannels can be produced with standard microfabrication methods and an active heat sink can be integrated as a second layer on top of the reaction microchannel. Therewith, 2D microchannels are good structures for a first microreactor that can be improved by 3D structures in future microreactor iterations, if required.

![Figure 5-3: These pictures show the principle of dean vortices in curved microchannels in a cross sectional view. (a) Typical vortex pair in a meander microchannel. (b) Movement of a gas bubble in the vortex pairs.](image)

The presented requirements of the microreactor for the reaction microchannel are sufficient mixing and an effective heat transfer out of the liquid. Furthermore, the liquid has to flow around the bubbles to provide a good convection at the gas-liquid interface. The following subchapter refer to the actual state of the art of 2D meander microchannels and to the state of knowledge within the working group [1]. The meander microchannels with the best performance were simulated in computational fluid dynamics (CFD) with similar design rules to compare the mixing quality, the wall contact and the Nusselt number for optimized heat transfer. Furthermore, the bubble trace in relation to the liquid flow was examined with a simple CFD simulation model.

**State of the art**

The groups of Jiang [2] and Schönfeld [3] have analyzed rectangular meander microchannels, formed as large bends, concerning their mixing quality and the effect of dean vortices. Another meander shape was investigated at small Reynolds numbers ($Re = 50$) by the group of Ehrfeld with microchannels, forming a square wave [4, 5]. The zigzag-formed meander variant was described by Mengeaud et al. with regards to the mixing quality depending on the length of the straight channels [6]. Nonino et al.
compared the mixing quality of different meander elements [7]. These were large s-formed bends, square waves and zigzag microchannels with 90° angles. The structures had the same quadratic cross section, a similar pitch of the meander and the same amplitude of the center line. The simulations were done for Reynolds numbers of $Re = 50-150$. As one main result the zigzag showed the lowest mixing performance. The s-formed bends and the square wave had a better mixing quality. However, the square wave had a higher pressure drop along the microchannel. Within our group Dreher investigated in his thesis the mixing and wall contact performance in meander microchannels for a broad range of Reynolds numbers [1]. His work compared mainly s-formed meander channels, wavy channels, omega (Ω) shaped channels, and zigzag microchannels. He combined different characteristics of these meander forms in his experiments and CFD simulations. As a result, he developed a dead zone-reduced zigzag meander optimized for microreactors and multiphase flow. This zigzag channel (with 90° or 60°) had rounded corners and exhibits a geometric focusing in the straight parts of the meander. This results in an optimized mixing and maximum wall contact due to the reduced dead zones in the microchannel. For the application in a microreactor with gas-liquid flow reduced dead zones are of decisive importance to avoid trapping of gas bubbles.

**Simulation conditions**

Nonino et al. [7] have compared s-formed bends, the square waves and the zigzag microchannels concerning their mixing performance. Furthermore, Dreher [1] developed a dead zone-reduced zigzag meander channel. Simulations were made to transfer the results of these two studies to the requirements of the aspired direct fluorination microreactor. The requirements were 2D microchannels with a cross section of 300 μm × 300 μm. The Reynolds number was at $Re = 150$ and the track of a 100 μm wide bubble was analyzed. This bubble size allows to determine the influence of dead zones in the meander channels on the flowing microbubbles.

All meander channels were simulated in CFD-ACE+ 2008.2 (ESI Group). The respective gas-liquid system was assumed with laminar flow. The mixing and the wall contact efficiency were simulated with the “flow” and the “scalar” module. To calculate the approximate interface shape of the bubble, the “volume of fluids” (VOF) module was used. For the surface reconstruction a piecewise linear interface construction (PLIC) was applied. The transient calculation was controlled and automatically adjusted to match the Courant-Friedrichs-Lewy (CFL) number. This CFL number was set to 0.2, which limits the interface progress to only 20% of one cell per time step. The transient multiphase simulations took 5 to 7 days CPU time on a Windows (XP Professional 64bit) personal computer with a Dual 3 GHz Intel Core2 processor with 8 GB RAM. The mixing performance, wall contact and the bubble trace were analyzed with images of the CFD-VIEW (ESI Group) software.

In the presented numerical study, the s-shaped bend, the square wave, the zigzag channel, and the optimized zigzag were simulated with a similar channel path length.
\( M = 1885 \, \mu m \). The meander amplitude \( W \) was designed such that \( M \) is similar for each meander variant. The amplitude refers to the centre of the channel. Following the design rules of Nonino et al. [7] and Menagud et al. [6], the meander axis length was \( L = 4W \). All meander channels had the same cross section with the hydraulic diameter \( d_H = 300 \, \mu m \). The optimized zigzag varied in cross section compared to the other designs due to the different design criteria with the bends and the flow focusing in the straight channel parts. However, the \( d_H \) mean value of the optimized zigzag was similar with the other meander channels. Table 5-1 summarizes the dimensions of the different meander designs that are illustrated in Figure 5-4. Considering that the fastest variance of the velocity was expected at the smallest meander radii the grid was meshed finest in this region. The smallest cell

<table>
<thead>
<tr>
<th>meander</th>
<th>( M ) [( \mu m )]</th>
<th>( L ) [( \mu m )]</th>
<th>( W ) [( \mu m )]</th>
</tr>
</thead>
<tbody>
<tr>
<td>s-shaped</td>
<td>1885</td>
<td>1200</td>
<td>300</td>
</tr>
<tr>
<td>rectangular</td>
<td>1885</td>
<td>944</td>
<td>236</td>
</tr>
<tr>
<td>zigzag</td>
<td>1885</td>
<td>1332</td>
<td>333</td>
</tr>
<tr>
<td>opt. zigzag</td>
<td>1885</td>
<td>1256</td>
<td>314</td>
</tr>
</tbody>
</table>

Figure 5-4: This pictures show the different meander channel designs from the top: (a) s-shape, (b) rectangle, (c) zigzag, (d) optimized zigzag. The meander have the same channel length \( M \) and are characterized with the meander axis \( L \) and the meander amplitude \( W \).
had a cubic side length of about 3 μm and the largest cell at the liquid outlet had a cubic side length of 10 μm. These mesh dimensions for the simulation of multiphase flow were proven in the simulations of the bubble generation in subchapter 2.4. Furthermore, the models with round walls have an increased number of cells and therefore more cells in sum, due to geometric design restrictions. This results in meshes with 465,150 cells for the s-shaped, 273,600 for the rectangular wave, 269,100 for the zigzag, and 540,900 for the optimized zigzag meander channel.

All meander channels were simulated for their mixing performance and wall contact efficiency. Toluene was provided to the inlet of the channel, with a parabolic flow profile and the outlet was set at 100 kPa. In one half of the channel inlet rhodamin B was added as a tracer. Rhodamine B is a typical fluorescence tracer with a diffusity of \( D = 2.8 \times 10^{-10} \text{ m}^2/\text{s} \). The normalized tracer concentration \( c \) characterizes the composition of the fluid. The concentration \( c = 1 \) indicates fluid with rhodamin B tracer and concentration \( c = 0 \) fluid without the tracer. A mixture of equal parts from both fluids has \( c = 0.5 \). The volume flow mixing quality is therefore defined as

\[
\alpha_V = 1 - \sqrt{\frac{ad^2(c)}{\hat{c}_V \cdot (1 - \hat{c}_V)}}, \tag{5.1}
\]

where \( \hat{c}_V \) is the mean value of the concentration over the volume flow \( \dot{V} \) and with variance of normalized concentration

\[
ad^2(c) = \frac{1}{V_{tot}} \int_{V_{tot}} (c - \hat{c}_V)^2 \, d\dot{V}, \tag{5.2}
\]

that is calculated over the total volume flow \( V_{tot} \) through the channel outlet. For the comparison of meander structures, Dreher [1] introduced a wall contact efficiency \( WE \) for the performance of heat exchanger. This efficiency is defined as the ratio of the benefit of the process and the effort that is necessary. For the wall contact, the Stanton number

\[
St = \frac{Nu}{Re \cdot Pr} \tag{5.3}
\]

is taken as the benefit. In this formula \( Nu \) describes the Nusselt number for the characteristic heat transfer in the channel, \( Re \) the Reynolds number and \( Pr \) the Prandtl number. As part of the effort for the wall contact, the Euler number

\[
Eu = \frac{\Delta p}{\rho \cdot \bar{v}^2} \tag{5.4}
\]

describes the dimensionless pressure drop \( \Delta p \) over the meander for the fluid with a density \( \rho \) and a mean velocity \( \bar{v} \). This leads to the definition of the wall contact efficiency
and is additionally normalized to a dimensionless number by the hydraulic diameter $d_H$ and the length of the channel $M$. The detailed equations and the simulation conditions for the mixing performance and the wall contact efficiency are described in detail in the thesis of Dreher [1].

For the transient simulations with the moving bubble, toluene flowed through the inlet and fluorine gas was used for the pre-placed bubble. A parabolic velocity profile of the liquid was generated at the inlet of the channels. The liquid flowed with a volume flow rate of 105 ml/h which resulted in a Reynolds number of $Re = 150$. The gas bubble with a diameter of 100 μm was placed 20 μm above the channel bottom. This is a characteristic position of a simulated bubble after the generation from a KOH nozzle, see chapter 2. The bubble started 150 μm downstream of the inlet at the beginning of all simulations. The pressure at the outlet was set at 100 kPa. All remaining geometrical boundaries were defined as walls. No-slip conditions were assumed at the walls. The wall contact angle for the gas-solid-liquid interface was set to $15^\circ$ for all surfaces. For other physical data of the fluids at room temperature see Table 5-2.

**Simulation results**

The mixing, wall contact performance, and the heat transmission of the simulated meander channels verified the trends of the state of the art and are listed in Table 5-3. The s-shaped meander shows the best wall efficiency $WE = 34.6 \times 10^{-3}$ in combination with the lowest pressure difference $\Delta p = 629$ Pa. For the volume-based mixing performance the zigzag meander shows an exceptionally high value at $\alpha_V = 0.47$. The price for this mixing

### Table 5-2: Physical parameters of the fluids used for the meander CFD simulations at 25 °C [8].

<table>
<thead>
<tr>
<th>parameter</th>
<th>symbol</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>viscosity – toluene</td>
<td>$\eta_{tol}$</td>
<td>$560 \times 10^{-6}$ Pa s</td>
</tr>
<tr>
<td>viscosity – fluorine</td>
<td>$\eta_f$</td>
<td>$22.6 \times 10^{-6}$ Pa s</td>
</tr>
<tr>
<td>density – toluene</td>
<td>$\rho_{tol}$</td>
<td>$866.9$ kg/m$^3$</td>
</tr>
<tr>
<td>density – fluorine</td>
<td>$\rho_f$</td>
<td>$3.15$ kg/m$^3$</td>
</tr>
<tr>
<td>interfacial tension (fluorine-toluene)</td>
<td>$\sigma$</td>
<td>$27.8 \times 10^{-3}$ N/m</td>
</tr>
<tr>
<td>wall contact angle (fluorine-toluene-silicon)</td>
<td>$\theta$</td>
<td>$15^\circ$</td>
</tr>
<tr>
<td>diffusity – rhodamin B</td>
<td>$D$</td>
<td>$2.8 \times 10^{-10}$ m$^2$/s</td>
</tr>
</tbody>
</table>
quality is a high pressure loss of $\Delta p = 1264$ Pa that is not preferred for a microreactor. The rectangular meander shows an overall good performance, but with large dead zones in the corners. However, the summarized performance of the optimized zigzag is the best of all meander channels. The Nusselt number of the optimized zigzag is the highest of all four structures with $Nu = 13.6$ and the mixing quality, wall efficiency and pressure loss are comparable with the respective best structures. Moreover, the optimized zigzag shows the smallest dead zones of all meander channels, which is preferred for the bubble flow in the channel. Figure 5-5 shows the simulated structures with cross sections at the beginning (A), the middle (B), the end (C) of the meandering structure and in the outlet channel (D). These cross sections display the concentration field of rhodamin B, indicating the mixing performance at the different channel sections. This demonstrates that the mixing performance is the best in the zigzag meander channel, followed by the rectangular and optimized zigzag channels. Moreover, the cross sections indicate the vortex pairs in the meander channels generated by the dean flow.

All meander variations were simulated in transient models to monitor the bubble movement within the flowing liquid. It turned out that the bubble flows along the channel length $M$ and rises within the lower dean vortex into the main flow and, hence, to the middle of the channel. The bubble remains there and is still mainly in the lower vortex but also touches the upper vortex. This increases the liquid flow around the bubble and, therefore, the reaction performance. Hence, the diffusion length around the bubble is reduced and additionally an increased amount of toluene molecules could react with the fluorine of the bubble. This effect accelerates the reaction time and increases the selectivity of the direct fluorination, where only one fluor- per toluene-molecule was preferred. This is also the case for the direct fluorination of EC. Furthermore, the mixing around the bubble enhances the heat dissipation away from the gas-liquid interface and avoids hot spots. The bubble height, meaning the distance to the channel bottom, did not differ substantially for the meander variations except for the optimized zigzag meander. Within this meander the bubble height fluctuates from the position between the two Dean vortices and near the channel bottom due to the flow focusing in the channel tapering. However,

<table>
<thead>
<tr>
<th>meander</th>
<th>$\alpha_\psi$</th>
<th>$WE$</th>
<th>$Nu$</th>
<th>$\Delta p$</th>
</tr>
</thead>
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<tr>
<td>s-shaped</td>
<td>0.34</td>
<td>$34.6 \times 10^{-3}$</td>
<td>11.6</td>
<td>629 Pa</td>
</tr>
<tr>
<td>rectangular</td>
<td>0.41</td>
<td>$27.8 \times 10^{-3}$</td>
<td>13.3</td>
<td>826 Pa</td>
</tr>
<tr>
<td>zigzag</td>
<td>0.47</td>
<td>$22.2 \times 10^{-3}$</td>
<td>12.3</td>
<td>1264 Pa</td>
</tr>
<tr>
<td>opt. zigzag</td>
<td>0.39</td>
<td>$31.0 \times 10^{-3}$</td>
<td>13.6</td>
<td>796 Pa</td>
</tr>
</tbody>
</table>
the transverse velocity field of the two zigzag channels shows the highest intensity. This means, a higher liquid flow around the bubble and, hence, favorable conditions for the direct fluorination. The bubble movement and the transverse velocity profile are exemplarily shown in Figure 5-6 at the beginning (A), middle (B), and end (C) of the meander structure.

The comparison of the four meander variations with CFD simulations show the advantage of the optimized zigzag meander. The heat transition was maximal with $\text{Nu} = 13.6$ and the performance of pressure loss, wall contact efficiency and mixing were comparable to the respective best meanders without the disadvantage of big dead zones. Moreover, the transient simulation has shown that the optimized zigzag generates a high convection around the bubble. That proves, that the optimized zigzag is the best meander structure for the direct fluorination microreactor.

**Reaction channel – meander design**

The knowledge gained from the simulations was implemented into the reaction microchannel design. The reaction channel is at the beginning a straight channel with a cross section of $300 \mu m \times 300 \mu m$ and length of $14.7$ mm before the gas bubbles are injected through the nozzle. This channel length was used to cool down the injected liquid
to the adjusted temperature of the chemical reaction. After the nozzle, the reaction channel continues with an optimized zigzag structure and a total length of 10.4 cm, see Figure 5-7a. The whole reaction channel has 44 bends and is separated into 7 longer sections. These sections were orientated perpendicular to the cooling channels of the active heat sink, see Figure 5-7b. The detailed view of the optimized zigzag is displayed in Figure 5-7c with a curved and straight channel part. The opening angle of the zigzag was 60°, see Figure 5-7d. The radii of the inner (100 μm) and outer (400 μm) channel wall in the curved part, as displayed in Figure 5-7e were horizontally shifted by 35 μm which resulted in a contraction of the 300 μm wide channel to 265 μm at one side and an expansion at the other side to a width of 335 μm. This affects also the straight channel parts in Figure 5-7f.

With this design of the reaction microchannel, it is possible to provide optimal heat transfer out of the liquid due to the wall contact efficiency and enhanced mixing of the liquid around the co-flowing microbubbles. Moreover, the mixing around the bubbles improves the heat transfer away from the gas-liquid interface where the maximum

Figure 5-6: These pictures show a gas bubble in the meander channel variations: (a) s-shape, (b) rectangle, (c) zigzag, (d) optimized zigzag. The bubble is shown at the three different sections as shown in Figure 5-5; at the beginning (A), the middle (B), the end (C) of the meander channels. The transverse velocity fields are indicated with arrows and show the dean flow intensity in the channels. This indicates also the mixing around the bubbles.
5.2 Design

Direct fluorination of toluene or other organic solvents are very fast and exothermic reactions. The reaction of fluorine gas with toluene has an excessive heat generation of $\Delta H = 470 \text{ kJ/mol}$. Furthermore, first temperature measurements in the minireactor during direct fluorination of toluene had shown a reaction time under 36 ms. Therefore, it is important to consider the heat generation associated with the direct fluorination, which has an effect on the selectivity of the reaction or, in worst case, can cause a runaway reaction. Microfabricated heat sinks can provide increased heat transfer to minimize these effects due to their high surface-to-volume ratio. With a combination of the micro heat sink and a reaction microchannel that is optimized for heat conduction out of the channel,

Figure 5.7: This figure shows (a) the fluidic chip with the whole reaction channel and (b) illustrates the combination of the reactor channel with the active heat sink on top. The detailed view of the reaction channel as optimized zigzag is shown in (c) with the curved (A) and the (B) straight channel part. (d) Shows the opening angle of the zigzag and (e), (f) show the dimensions of the channel parts (A) and (B), respectively.

temperature rise originates. All removed heat has to be distributed with the active heat sink, which is presented in the following subchapter.

5.2.3 Active heat sink
the heat can be removed efficiently from the reaction site.

The reaction channel design was already shown in the previous subchapter. In the following, the state of the art of micro heat sinks is presented with common systems and established configurations. This leads to a heat sink design for the direct fluorination microreactor in silicon layer 3 of the microreactor, see Figure 5-1. That design is calculated in a worst case scenario to investigate the theoretical heat flux performance during a direct fluorination reaction in the microreactor.

State of the art

The market for technological applications, which require a high rate of heat flux removal on relatively small spaces increased rapidly since 1980 [9]. Developments in semiconductor technologies and advanced very large scale integration (VLSI) led to higher levels of integration and increased heat fluxes per area in these devices [10]. Beneath the important topic of CPU cooling, a number of other application fields need high rates of heat transfer such as optical, microwave or nuclear systems [11]. Furthermore, with the miniaturization of pharmaceutical, chemical and petrochemical reactors, the heat transfer in small spaces is a rising key issue for this applications [12]. One potential solution for the thermal management of small systems are microchannel heat sinks, which were first introduced by Tuckerman et al. [13]. They employed a direct circulation of water in microchannels in silicon chips and developed optimizations of the channel cross sections to increase the heat flux and to decrease the pressure loss. Upadhye et al. presented a detailed overview of microchannel optimization for micro heat sinks [14].

There is much interest to understand the fluid flow and heat transfer characteristics in silicon-based micro heat sinks. Over the last decades many investigations were reported but still there is no convincing explanation of the difference between experimental and theoretical results [10]. Sobhan et al. [15] and Hetsroni et al. [16] presented comprehensive reviews of the conducted investigations.

There are several methods reported to increase the Nusselt number of the microchannels. These are designs with large aspect ratio channels [13], geometric obstructions like fins [17], biomimetic tree-like bifurcation channels [18, 19], serpentine channels to promote mixing and turbulence [20], two-phase flow [21], and short channels where the entrance region dominates [22, 23]. For most of the micro heat sinks the design of parallel microchannels are used to facilitate a homogeneous heat flux over a large area [24, 12]. For parallel microchannels the uniform flow distribution plays an important role. Otherwise, it can lead to span-wise heat flux gradients [25]. Hence, it is necessary to optimize the manifold configuration. Mishan et al. [25] and Commenge et al. [26] proposed several manifold designs to optimize the flow distribution in the parallel microchannels.

Micro heat sinks in microreactors are used for rapid heat transfer between hot and cold liquid [12]. Therewith, it is important that the hot and cool fluid flow in a co-current, counter-current or cross-current mode, see Figure 5-8. These flow modes have an influence on the heat flux efficiency over the whole heat sink. The co-current mode is most efficient
5.2 Design

at the beginning, whereas the counter-current mode distributes the heat flux over the whole heat sink and reaches better cooling efficiency [27]. The cross-current heat mode allows a constant temperature distribution over the whole channel length and is the most used configuration [12, 28, 29, 30].

Heat sink design

Direct fluorination is a chemical reaction that is very fast and occurs mainly at the beginning of the reaction channel. For this case a co-current or cross-current flowing multichannel heat sink can prevent hot spots at the beginning and allows also a homogenous temperature distribution over the whole cooling area. Furthermore, Qu et al. [23] reported an entrance effect, with higher heat fluxes i.e. higher Nusselt numbers at the channel inlets. This effect occurs due to the thin thermal boundary layers in the flow developing region. These considerations lead to the heat sink design of the microreactor shown in the following.

The active heat sink is realized in silicon layer 3. It covers the complete reaction microchannel with an array of 21 parallel, 12 mm long minichannels with cross sections of 300 μm × 300 μm, see Figure 5-9. Channel cross sections with a much higher aspect

Figure 5-8: Schematic of the three flow modes of an active heat sink. The cooling flow can be in the same direction (co-current), in the opposite direction (counter-current), and perpendicular direction (cross-current) relative to the hot flow.

Figure 5-9: Schematic sketch of the active heat sink for the microreactor. The heat sink consists of an inlet that flows into the inlet chamber (A). This chamber connects the cooling channel array (B) and is 2.1 mm wide at the first channel and narrows to 100 μm at the last channel. Each cooling channel has a cross section of 300 μm × 300 μm and flows into the outlet chamber (C) and the outlet.
ratio of width and height would perform better heat fluxes [13, 14] but with a higher risk of clogging due to particles. The spatial relation between the reaction channel and the active heat sink is depicted in Figure 5-7b. All channels are divided by 300 μm thick walls and run perpendicular to the longer sections of the of the reaction microchannel. Therewith, the cooling at the first part of the reaction channel is in cross-current mode for effective cooling. This first section of the reaction microchannel is also located at the beginning of the parallel channel array with higher heat fluxes due to the entrance effect. Over the whole length of the reaction microchannel, the cooling flow is mainly in co-current mode. Hence, the cooling ratio is most efficient near the gas injection where most of the heat is generated due to the chemical reaction.

The material thickness between the reaction channel and the cooling array is 225 μm. The manifolds at the inlet and at the outlet of the heat sink are designed to form a continuous liquid distribution for all cooling channels. These design rules were reported by Commenge et al. [26]. Inlet and outlet chambers for the cooling array are 2.1 mm wide and narrow down with a 9° angle to 100 μm at the last cooling channel.

Calculations
Heat transfer in a microsystem with a hot reaction channel and a microstructured active heat sink is following a highly complicated scheme with non-uniform distribution of all thermal characteristics [12]. These systems can be analyzed with numerical simulations as shown by Tiselj et al. [31] and Mishan et al. [25] with manifolds and parallel microchannels in CFD. In most cases, the numerical calculations of these complex thermal systems require a high computational effort and have still uncertainties for complex systems like microreactors. Furthermore, the reaction behavior of direct fluorination is not examined to determine the heat generation over the whole length of the reaction channel. However, simplified calculations with a worst case scenario were done within this thesis with reasonable effort and outcome to determine the minimum requirements of the active heat sink.

For a calculation of the active heat sink, the generated heat of the reaction is important. The microreactor is designed for a reaction of liquid toluene with fluorine gas. For the calculations, concentrations of 100% toluene in the liquid and 100% fluorine in the gas are assumed. The liquid flow of 70 ml/h and the gas flow of 30 ml/h facilitate a reliable generation of monodisperse microbubbles. With the 20 μm × 80 μm KOH microreactor nozzle and the described fluid flow rates, bubbles of 198 μm diameter can be generated with a frequency of 1400 Hz (see subchapter 2.5). The gas is assumed as incompressible due to the low Mach number \((Ma < 0.3)\) [27]. Thus, the total volume flow after the gas bubble injection was 100 ml/h which is the intended throughput of the microreactor. With a channel length of 104 mm and a mean channel cross section of 300 μm × 300 μm, the residence time in the reactor is 0.34 s. With that residence time, the whole fluorine gas is supposed to react within the microreactor. This means that the whole heat of the reaction is fed into the microreactor system. With the gas flow of 30 ml/h, the molar
5.2 Design

The volume flow of fluorine is \( \dot{n}_{F_2} = 0.371 \times 10^{-6} \text{ mol/s} \). The heat of reaction is \( \Delta H = 470 \text{ kJ/mol} \) [32] for the reaction of fluorine with toluene. Therewith, the amount of the generated heat flux is \( Q = 0.17 \text{ W} \) in the microreactor for the conditions given above. The heating of the reaction medium \( \Delta T_{tol} \) within the reactor can be determined with

\[
\Delta T_{tol} = \frac{\dot{Q}}{\dot{V}_{tol} \cdot \rho_{tol} \cdot c_{p,tol}},
\]

where \( \dot{V}_{tol} \) is the volume flow rate, \( \rho_{tol} \) the density, and \( c_{p,tol} \) the heat capacity of toluene at room temperature. All physical constants are enlisted in Table 5-4. The heat conduction of the gas is neglected. With the calculated heat flux \( \dot{Q} \) the temperature rise in the reaction medium is \( \Delta T_{tol} = 5.91 \text{ K} \). This temperature increase is present without an active cooling and only in the liquid toluene. When it is assumed that the heat is only absorbed by the liquid reactant and the cold flow of water in the heat sink, the temperature can be calculated with:

Table 5-4: This table summarizes the physical constants of water and toluene at room temperature (25 °C) for the thermal calculations. The labeling water (w) also indicates the cooling channel and toluene (tol) the optimized zigzag meander.

<table>
<thead>
<tr>
<th>parameter</th>
<th>symbol</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>molar volume – fluorine</td>
<td>( V_{m,F_2} )</td>
<td>0.0224 m³/mol</td>
</tr>
<tr>
<td>reaction heat – fluorine/toluene</td>
<td>( \Delta H )</td>
<td>470 kJ/mol</td>
</tr>
<tr>
<td>density – toluene</td>
<td>( \rho_{tol} )</td>
<td>867 kg/m³</td>
</tr>
<tr>
<td>density – water</td>
<td>( \rho_w )</td>
<td>998 kg/m³</td>
</tr>
<tr>
<td>heat capacity – toluene</td>
<td>( c_{p,tol} )</td>
<td>1707 J/(kg·K)</td>
</tr>
<tr>
<td>heat capacity – water</td>
<td>( c_{p,w} )</td>
<td>4185 J/(kg·K)</td>
</tr>
<tr>
<td>thermal conductivity – nickel</td>
<td>( \lambda_{Ni} )</td>
<td>91 W/(m·K)</td>
</tr>
<tr>
<td>thermal conductivity – silicon</td>
<td>( \lambda_{Si} )</td>
<td>150 W/(m·K)</td>
</tr>
<tr>
<td>thermal diffusivity – toluene</td>
<td>( \alpha_{tol} )</td>
<td>5712 W/(m²·K)</td>
</tr>
<tr>
<td>thermal diffusivity – water</td>
<td>( \alpha_w )</td>
<td>10,692 W/(m²·K)</td>
</tr>
<tr>
<td>Prandtl number – water</td>
<td>( Pr_w )</td>
<td>6.99</td>
</tr>
<tr>
<td>Nusselt number – toluene</td>
<td>( Nu_{tol} )</td>
<td>13.5</td>
</tr>
<tr>
<td>Nusselt number – water</td>
<td>( Nu_w )</td>
<td>5.28</td>
</tr>
</tbody>
</table>
\[ \Delta T_{\text{tol,w}} = \left( \frac{\dot{V}_{\text{tol}} \cdot \rho_{\text{tol}} \cdot c_{p,\text{tol}} + \dot{V}_{w} \cdot \rho_{w} \cdot c_{p,w}}{\Delta H \cdot \dot{n}_{F_2}} \right)^{-1}. \]  

The constants \( \dot{V}_{w}, \rho_{w}, \) and \( c_{p,w} \) are the volume flow, density and the heat capacity of water at room temperature, respectively. With a cooling volume flow of \( \dot{V}_{w} = 400 \text{ ml/h}, \) the total temperature increase is only \( \Delta T_{\text{tol,w}} = 0.37 \text{ K}. \)

However, these global calculations do not consider the problems of the heat conduction out and into the liquid media and through the solid walls between the liquids. A simple thermal model explains the heat flux between the hot reaction channel and the cool active heat sink. Figure 5-10 shows a schematic sketch of the thermal system and a thermal resistance model with the convective and conductive resistances. The heat flow out of the heated toluene into the surrounding nickel wall. From the nickel wall, the heat flows through the silicon and over the next nickel wall of the heat sink and then into the cooling water flow. The thermal radiation is neglected for this application. To calculate the thermal resistances, several simplifications for worst case are done. The convective resistance out of the reaction channel \( R_{\text{tol-Ni}} \) is calculated with the surface area of three walls \( (A_{\text{tol}} = 93.6 \text{ mm}^2) \) and the Nusselt number \( (Nu_{\text{tol}} = 13.6) \) of the optimized zigzag meander.

---

**Figure 5-10:** (a) This sketch shows a side view of the reactor with the channel for the heat flow lengthwise and for the cooling flow crosswise. The heat \( \dot{Q} \) flows from the reaction channel through the solid walls into the cooling flow. This is indicated in (b): The resistance indices stand for the convective resistance from the heated toluene into the nickel channel wall (tol-Ni) and from the nickel channel wall into the cooling water (Ni-w). The conductive resistances are present in the nickel wall and in the silicon substrate (Ni, Si), respectively.
simulations, see subchapter 5.2.2. The active heat sink is an array of 21 cooling channels, that are 12 mm long and exhibit channel cross sections of 300 μm × 300 μm. For the convective resistance into the cooling water $R_{Ni-w}$ the surface area ($A_w = 226.8$ mm$^2$) is taken as a sum of all parallel channels where only three walls are considered, respectively. The Nusselt number for laminar water flow in straight microchannels is calculated with the classical approach [33]

$$Nu = 0.664 \cdot \sqrt[3]{Re} \cdot Pr,$$

for the quadratic cross section dimensions of 300 μm × 300 μm. For a total cooling volume flow of 400 ml/h the Reynolds number is $Re = 17.6$ per cooling channel. With the Reynolds number and the Prandtl number $Pr = 6.99$ [33] results the Nusselt number of $Nu_w = 5.28$. Both conductive resistances of the nickel layers $R_{Ni1}$ and $R_{Ni2}$ are calculated with the surface areas of the reaction channel and the cooling channels, respectively. The conductive resistance of silicon $R_{Si}$ is simplified to the area which is covered with the parallel cooling channel array without the manifolds ($A_{Si} = 148$ mm$^2$). The thicknesses for the thermal resistances are 225 μm for the silicon layer, 27 μm for the reaction channel and 10 μm for the cooling channels nickel layer. Therewith, the temperature increase can be calculated with:

$$T_{in} - T_{out} = \Delta T_{sum} = (R_{tol-Ni} + R_{Ni1} + R_{Si} + R_{Ni2} + R_{Si-w}) \cdot \dot{Q}.$$  

The thermal resistances listed in Table 5-5 show the range between convective and conductive resistances. The conductive resistances are negligible in this microsystem due to the small thickness and large areas of the separating silicon and nickel walls. This demonstrates the importance of the proper fluidic design to increase the Nusselt number and, therefore, decrease the conductive resistance. The temperature increase of the system results with all resistances in $\Delta T_{sum} = 0.39$ K. This is insignificantly higher than the temperature increase $\Delta T_{tol,w}$ if only the liquids absorb the heat energy. However, this model is calculated with the assumption that the reaction heat is distributed over the whole reactor system.

**Table 5-5:** This table summarizes all thermal resistances of the microreactor when the reaction heat is dissipated over the whole reaction channel length.

<table>
<thead>
<tr>
<th>thermal resistance</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{tol-Ni}$</td>
<td>1871 mK/W</td>
</tr>
<tr>
<td>$R_{Ni1}$</td>
<td>3 mK/W</td>
</tr>
<tr>
<td>$R_{Si}$</td>
<td>10 mK/W</td>
</tr>
<tr>
<td>$R_{Ni2}$</td>
<td>1 mK/W</td>
</tr>
<tr>
<td>$R_{Ni-w}$</td>
<td>412 mK/W</td>
</tr>
</tbody>
</table>
The direct fluorination is a very fast reaction and the reaction time depends only on the diffusion of fluorinated toluene away from the interface where the reaction occurs to be replaced by a non-reacted toluene molecule. Therefore, the diffusion time of toluene away from the bubble interface is calculated. For the calculations, the physical properties of toluene and fluorinated toluene are assumed to be identical. The diffusion model is an unidirectional diffusion with an inexhaustible source of a sphere, which is in this case the gas bubble. As worst case scenario, the spherical bubble is assumed to be permanently in the same size and disappears with the complete diffusion of the volume. The diffusion flux for this case is given by \[ [34] \]

\[
j_{\text{tol}} = \frac{D_{\text{tol}}}{r_0} \cdot c_{\text{tol}}(\text{sat}) \tag{5.10}
\]

where \( D_{\text{tol}} \) is the diffusion constant of toluene and \( c_{\text{tol}}(\text{sat}) \) the saturated concentration of toluene (\( D_{\text{tol}} = 1.85 \times 10^{-5} \text{ cm}^2/\text{s} \) [34]; \( c_{\text{tol}}(\text{sat}) = 9423 \text{ mol/m}^3 \)). Due to the optimized convection around the bubble, the radius \( r_0 \) for the saturated concentration is the same as the bubble radius. For the reaction conditions and with a \( 20 \mu\text{m} \times 80 \mu\text{m} \) KOH nozzle, the bubbles have a radius of 99 \( \mu\text{m} \). Therewith, results the diffusion flux away from the bubble to \( j_{\text{tol}} = 0.176 \text{ mol/m}^2\cdot\text{s} \), see Eq (5.10). This means, for the spherical surface around the bubble results with \( j_{\text{tol}} \) a diffusion rate of \( \dot{n}_{\text{tol}} = 21.7 \times 10^{-9} \text{ mol/s} \). The reaction scheme in Figure 5-11 displays the direct fluorination of toluene. It shows that one fluorine molecule is needed for the reaction with one toluene molecule. For a molar fluorine volume of \( n_{F_2} = 18 \times 10^{-11} \text{ mol} \) in one bubble, the total reaction time is \( t_{\text{reac}} = 9 \text{ ms} \). This is significantly smaller than the residence time of \( 0.34 \text{ s} \) in the reactor. The channel length where the whole reaction is completed is \( l_{\text{reac}} = 2.8 \text{ mm} \) for a volume flow rate of 100 ml/h. In that case the whole heat is generated in this short part of the channel and the heat sink has to be able to remove this heat to avoid hot spots. This short section of the reaction channel results in smaller areas and hence bigger thermal resistances for the heat dissipation. The small areas are calculated according to the surface areas valid for the whole reactor but only for the shorter length \( l_{\text{reac}} \). Therewith, the areas are: \( A_{\text{tol}} = A_{\text{Ni1}} = 2.52 \text{ mm}^2 \), \( A_{\text{w}} = A_{\text{Ni2}} = 3.6 \text{ mm}^2 \), and \( A_{\text{Si}} = 2 \text{ mm}^2 \). All thermal resistances

![Figure 5-11: Reaction scheme of direct fluorination of toluene.](image-url)
5.2 Design

for this short reactor length are listed in Table 5-6. The thermal increase [see Eq (5.9)]
results in $\Delta T_{\text{reac}} = 16.38$ K. This increase of the temperature in worst case is still tolerable
for the chemical reaction and proofs theoretically the efficiency of the active heat sink
design for the microreactor.

Table 5-6: This table summarizes all thermal resistances of the microreactor when the reaction
occurs only over a reaction channel length of $l_{\text{reac}} = 2.8$ mm.

<table>
<thead>
<tr>
<th>thermal resistance</th>
<th>value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{\text{tol-Ni}}$</td>
<td>52.11 K/W</td>
</tr>
<tr>
<td>$R_{\text{Ni1}}$</td>
<td>0.12 K/W</td>
</tr>
<tr>
<td>$R_{\text{Si}}$</td>
<td>0.75 K/W</td>
</tr>
<tr>
<td>$R_{\text{Ni2}}$</td>
<td>0.03 K/W</td>
</tr>
<tr>
<td>$R_{\text{Ni-w}}$</td>
<td>19.48 K/W</td>
</tr>
</tbody>
</table>

5.2.4 Reactor platform

The main task of the reactor platform is to connect the silicon microreactor with the conventional gas and liquid tube fittings and to seal the reactor system gas tight. The platform consists of three copper plates: the fluidic connection plate, the fluidic plate, and the cooling plate. All copper plates were covered with fluor resistant nickel after machining. The design was based on the experiences made with the minireactor system. The minireactor experiments had shown, that it is important to realize the tapped holes for the tube fittings in a plate separate from a second plate that carries the borings that connect the silicon microreactor. That means, the tube fittings in the fluidic connection plate press o-ring gaskets made of teflon on the back side of the fluidic plate with borings of 1 mm diameter. These borings are connected to the reaction channel in the silicon microreactor with the liquid inlet, gas inlet and the product outlet. This configuration is important because of the used fluorine gas. The cooling connection with a drilled boring (1 mm) and the tapped hole for the tube fitting are combined in a single cooling connection plate. The boring and the inlet/outlet of the microreactor heat sink are connected with O-ring gaskets. For the assembly of the complete reactor system, the microreactor is located between the fluidic plate and the cooling plate and aligned with a recess in the cooling plate. The fluidic connection plate is placed on the backside of the fluidic plate and all three parts are screwed together. Afterwards the whole reactor system is sealed with a nickel layer within the fluidic system and a nickel layer on the complete outer surface of the microreactor and reactor platform. A schematic side view of the microreactor combined with the reactor platform is shown in Figure 5-12.
5.3 Fabrication

The fabrication of the microreactor for direct fluorination can be divided into two main parts, which are the microfabrication of the silicon chips with the microstructures and the machining of the fluidic platform made of copper. The silicon microreactor and the platform are assembled to a complete microreactor system by, screw mounting, electroplating and electroless plating.

5.3.1 Microreactor

The microfabrication process to produce the microreactor and the bonding to the fluidic platform is schematically illustrated in Figure 5-13. The three basic unit operations, i.e. the bubble generation, mixing/heat transfer, and heat dissipation with active heat sink were placed in three different 525 μm thick, double side polished <100> silicon substrates. The nozzle for the bubble generation was machined with potassium hydroxide (KOH) etching and the reaction and cooling channels were fabricated with deep reactive ion etching (DRIE). The structured cooling and reaction channel, and the nozzle substrates are shown from their back side in the photographs of Figure 5-14.

For the KOH etching, the nozzle substrate was masked at the front and back side with silicon oxide (SiO₂) and silicon nitride (Si₃N₄). The SiO₂ was grown 300 nm thick by thermal oxidation. Over the SiO₂ layer a 100 nm Si₃N₄ was deposited by low-pressure chemical vapor deposition (LPCVD). The back side of the wafer was photolithographically patterned to define the nozzle. The exposed silicon nitride/oxide was etched with reactive
Figure 5.3 Fabrication

Figure 5-13: Fabrication process of the silicon microreactor (a), (b), (c) and the nickel plating with integration onto the fluidic platform (d), (e).
5 Microreactor

ion etching (RIE) to open the etch mask. Afterwards the nozzles were etched with KOH from the back side through the silicon wafer to the etch stop at the front side. This etching step fabricated a wide opening of the nozzle channel at the back side and a small, defined nozzle orifice at the front. The silicon nitride/oxide mask was afterwards removed by wet chemical etching with hydrofluoric acid (HF). This is depicted in Figure 5-13a, b.

A 4000 nm thick SiO₂ layer was thermally grown on the back side of the reaction channel substrate and the cooling substrate. A photolithographic step defined the microchannels. After opening the SiO₂ masking layer with RIE, the channels were etched 300 μm deep with DRIE, see Figure 5-13a, b. Afterwards, the oxide mask was removed with HF. To contact the active heat sink, the cooling substrate needed another etching step from the front-side of the cooling substrate. A new silicon oxide layer of 2.3 μm thickness was grown on the front side of the layer. As like for the back side the front side was photolithographically patterned and the oxide mask was opened with RIE (Figure 5-13a). Finally, the contact hole was etched 125 μm deep with a second DRIE step through the silicon to the cooling channels and the oxide mask is removed with HF (Figure 5-13b).

The structured substrates are coated at their front and back side with a vapor-deposited palladium seed layer (150 nm), see Figure 5-13c. A rapid thermal annealing of 225 °C for 3 min forms a palladium silicide interface between palladium and silicon and ensures an excellent adhesion of the seed layer to the silicon substrates. The fluidic structures in the silicon substrates were covered with a fluorine resistant nickel layer, as described in subchapter 3.3. Furthermore, this nickel layer bonds and seals the silicon substrates and the nozzle substrate to the fluidic platform made of copper. For the microreactor two plating steps were needed in total. First an in-channel electroless plating and second an electroplating on the surface of the assembled reactor system was performed. The

Figure 5-14: This picture shows (a) the microstructured cooling substrate, (b) the reaction channel substrate and, (c) the nozzle substrate from the back side. The chip side length are 2 cm × 2 cm.
pretreatment for the electroless plating was a hot electro-degreasing in sodium hydroxide (0.3% concentration, 75 °C, 30 s) and an acid pickling with hydrochloric acid. The acid had a concentration of 38% combined with ultra sonic treatment for 30 s at a temperature of 50 °C. This was done to remove the surface oxide layer immediately before the electroless plating. The fluidic structures were closed with the lid of the corresponding substrate. Afterwards, an electrolyte solution of electroless nickel was pumped through the fluidic system, see Figure 5-13d. The volume flow rate pumped into the reaction channel was 108 ml/h and the volume flow rate pumped through the nozzle was 18 ml/h. With these volume flow rates moderate Reynolds numbers between Re = 16 and Re = 117 occur at the nozzle orifice and in the reaction channel to guarantee a homogeneous nickel plating. The volume flow rate in the active heat sink was 137 ml/h (Re = 31 in the inlet and outlet chamber) in total. Therewith, an approximate volume flow rate of 6.5 ml/h (Re = 6) was achieved in each cooling channel. The electrolyte solution SurTec®833 (SurTec, Germany) was used for this process. The pumping occurred at 92 °C and with deposition rates of approximately 6 μm/h at a pH value between 4.6 and 5.2. The deposited nickel walls post-formed the fluid microchannels and additionally bonded the chip substrates together. Additionally, the nozzle substrate was bonded to the fluidic platform. The bond also facilitated a gas tight and continuous sealing between microchip and platform. The final nickel wall thickness of 27 μm at the reaction channel with the KOH nozzle and 10 μm in the cooling system were controlled by the deposition time.

To ensure a mechanically stable bond between all components, the fluidic platform for the nozzle and the silicon chips were coated with nickel in an electroplating step. The pretreatment was hot electro-degreasing in sodium hydroxide (10 s) and an acid pickling with hydrochloric acid (38% concentration, 50 °C) combined with ultra sonic treatment for 30 s. A 40 μm thick nickel layer was electroplated with Slotonik 50 (Schloetter, Germany) on top of the silicon chips with a palladium seed layer and the fluidic copper platform with a current density of 2 A/dm².

5.3.2 Reactor platform

The microreactor platform with the three layers, as shown in Figure 5-15, was conventionally machined into copper plates. These copper plates were coated with corrosion resistant nickel. After the assembly of the microreactor with the reactor platform, the system was coated and sealed gas tight with an additional nickel layer.

The recess in the cooling connecting plate to align the silicon microreactor was milled 300 μm deep into the 8 mm thick copper plate. At the position of the cooling inlet and outlet within this recess, the connecting holes (1 mm diameter) were provided and also the groove for the o-ring gasket. The o-rings were 1 mm thick and hence, the groove 800 μm deep. The connecting holes join at the other side with the tapped holes (size M5) for the tube fittings made of stainless steel (CRQS-M5-4, Festo, Germany). The 4 mm thick fluidic plate was machined with an ultra-precision micro milling machine (UPM) on the
top to provide a very smooth surface. This smooth surface is necessary to facilitate the nickel bond between the fluidic plate and the microreactor. In the fluidic plate, the connecting holes were drilled with a diameter of 1 mm and positioned under the gas and fluid inlets/outlet of the microreactor. Due to the fact that the inlets/outlet are only located with a distance of 8-10 mm, the Monel tube fittings (SS-200-1-2RP, Swagelok, USA) were not located directly under the connecting holes. To make room for the tube fittings, 1 mm deep and 1 mm wide slits were milled in the back side of the fluidic plate as channels for the liquid inlet and the product outlet. The gas inlet is the most critical part due to the presence of fluorine gas and, therefore, positioned directly above the connecting hole. The milled liquid inlet channel is 12 mm long and the product outlet channel is 22 mm long, both leading to the positions of the tube fittings. The channels were closed with the fluidic connection plate. The tapped holes for the Monel fittings were drilled through the fluidic connection plate. In every platform plate, four through holes (size M5) were drilled for the screws that hold the complete system together. After machining, all structured copper plates were electroplated with 5 μm thick high gloss nickel Slotonik 50 (Schloetter, Germany).

The platform plates and the microreactor were adjusted and fixed with screws. After the silicon microreactor and the platform plates were assembled, a nickel layer was deposited in every fluidic structure with the in-channel electroless plating described in subchapter 5.3.1. Furthermore, the complete reactor system was sealed with electroplating on the external surface with 40 μm thick nickel (Slotonik 50, current density: 2 A/dm²). The pretreatment for the electroplating and the electroless plating were a hot electro-degreasing in sodium hydroxide (0.3% concentration, 75 °C, 30 s) and an acid pickling with hydrochloric acid (30% concentration, 50 °C) for 1 min to remove the surface oxide layer on the microreactor structures and the platform plates.

Figure 5-15: The microreactor platform is a multilayer construction with (a) the cooling plate, (b) the fluidic plate, and (c) the fluidic connection plate.
5.4 Functionality tests

5.4.1 Bubble generation

The bubble generation performance of the 20 μm × 80 μm KOH nozzle was tested within the microreactor. The difference between the test nozzles and the microreactor nozzle was the fabrication and the material. The test nozzle was etched silicon, whereas the microreactor nozzle was etched silicon with plated nickel. Both nozzles had the same orifice of 20 μm × 80 μm size. For the measurements, the silicon chip with the reaction microchannel structure was replicated with an optically transparent material. This replica of the reaction microchannel layer was casted with transparent epoxy (Araldite 2020, Huntsman, Switzerland) using an intermediate PDMS mold. This allowed to observe the bubble formation with the microfluidic test setup as described in subchapter 2.5. The bubble generation was observed with a photodiode setup to detect the bubble generation frequency. The used liquid was 2-propanol and the gas was nitrogen. Measurements of this nozzle within the microreactor showed equivalent bubble generation frequencies and bubble sizes as described in chapter 2. The graph in Figure 5-16 displays the generated nozzle diameters for a fixed liquid flow of 50 ml/h and a gas flow rate variation from 9.7 ml/h to 60 ml/h. The reactor nozzle generated bubbles with a maximum variance of 7% due to size variations of the nozzle orifice. The nickel plating is not as precise as the KOH etching process and the nozzle orifice size can vary about 5 μm. Furthermore, the bubble generation of the reactor nozzle was not restricted to the gas flow rates between 20 ml/h and 36 ml/h like the test nozzle. The reactor nozzles produced monodisperse bubbles over the complete range of the gas flow rate from 9.7 ml/h to 60 ml/h. The reason for this could be the different fluidic connection of the test chip and the reactor chip. That can cause a different fluidic capacitance which seems to have an effect on the bubble generation.

5.4.2 Active heat sink

Flow distribution

Following the design rules of Commenges et al. [26] the active heat sink was designed with 21 parallel cooling channels that were fed by a narrowing inlet chamber. The outlet chamber was designed similarly but extends to the outlet channel. Studies of Klein et al. [35] and Mishan et al. [25] have shown the effect of the manifold design for the flow distribution among parallel microchannels. A variation of the flow distribution can lead to span-wise temperature gradients in the device [10]. Therefore, flow tests with fluorescein were performed to determine the uniform flow rate distribution in every cooling channel. Fluorescein has the absorption maximum at 489 nm and its emission maximum at 516 nm for the used saturated solution with pH = 11.5. For details of fluorescein and the according
test setups, see the work of Diehl et al. [36].

The active heat sink chip was covered with an optically transparent pyrex chip and the inlet and outlet were contacted with affixed conventional tubings. The inlets were fed with two syringe pumps (Injectomat 2000, Fresenius, Germany) coupled by a three-way valve. One pump was for deionized water and the other pump was used for the fluorescein solution. The cooling channels were observed through a microscope (BX51, Olympus, Japan) with the filter set XF100-3 (Melles Griot, USA) and a camera EOS 500D (Canon, Japan). The excitation filter passed only wavelengths of the light source lower than 500 nm while the emission filter passed only light with wavelengths higher than 500 nm. Therewith, only emitted light of fluorescein was detected with the camera. The measurement setup is schematically shown in Figure 5-17.

At the beginning of the measurements, the whole fluidic cooling structure was filled with water and no emitted light was detected. The water flow was stopped and the inlet supply was switched to the fluorescein source. The water in the cooling structure was displaced by the fluorescein solution. Hence, the interface between the two liquids can be detected by the emitted light intensity. The liquid flow rates of the fluorescein to fill the cooling structure were 100 ml/h, 200 ml/h, 300 ml/h, and 400 ml/h. The flow rates of 100 ml/h and 200 ml/h require 6 s and 4 s, respectively to fill every channel of the cooling structure. However, the cooling channels were filled one by one in the same time steps from the channel closest to the inlet to the channel next to the outlet. This behavior was caused by
the inflating liquid front in the inlet chamber. The stepwise flow distribution in a detailed view of 9 microchannels (see Figure 5-18a) is exemplarily shown at two time steps (1.5 s, 2.6 s) for 200 ml/h in Figure 5-18b. At higher liquid flow rates, the channels were filled more uniform in comparison to the lower flow rates. Due to the higher flow rates and the uniform flow distribution, the complete cooling structure was filled within 3 s and 2 s for flow rates of 300 ml/h and 400 ml/h, respectively. Figure 5-18c shows the flow distribution of the cooling channels for the liquid flow of 400 ml/h at 0.6 s and 1.7 s after the switch-over to fluoresceine. The channels were not filled stepwise as expected for the lower liquid flow rates, because the filling of the inlet chamber was much faster. This fast filling caused also vortices in the inlet chamber, which were the reason for the initially irregular filling of the channels in the first milliseconds.

Every measurement showed a complete filling of all 21 liquid channels without remaining liquid and with a similar filling time for each channel. This happened within seconds, depending on the liquid flow rate. The stepwise filling (for 100 ml/h and 200 ml/h) and the initially irregular filling (for 300 ml/h and 400 ml/h) were caused due to the inflating liquid front in the inlet chamber. However, the liquid flow rates in the parallel channels were equal as predicted by Commenge et al. [26]. This led to the conclusion, that the liquid flows through the cooling structure homogeneously and provides an uniform heat transfer.
The cooling efficiency of the active heat sink in the microreactor was determined with a simple measurement setup. The silicon microreactor substrates were bonded and sealed with the in-channel electroless plating and contacted with affixed conventional tubings. Afterwards, the whole microreactor was encapsulated with a 2 mm thick layer of thermally insulating epoxy (*Endfest 3000*, Uhu, Germany). Furthermore, the whole chip was embedded in a thermally insulating polystyrene box. Two syringe pumps (*Injectomat 2000*, Fresenius, Germany) were connected to the test chip to feed the heating and cooling liquids. At the inlets and outlets, the temperatures of the liquids were measured with thermo elements (*Type T*, Labfacility, UK). The thermo elements were connected to a voltmeter (*NI 9219*, National Instruments, USA), and analyzed using a programmed virtual instrument (*Lab-View*, National Instruments, USA). The temperatures were determined with a mean temperature value taken from 100 measurements during 100 s. The thermal setup is schematically shown in Figure 5-19.

For the thermal measurements, the reaction microchannel was fed with 70 °C hot water and the cooling channels with 28 °C cold water. Highly demanding cooling situations, like in a microreactor, are typically managed with water instead of air or fluorochemical liquids as a coolant [10, 37]. The heated flow rate was fixed at 100 ml/h and 200 ml/h and the cooling flow rate was varied between 10 ml/h and 1000 ml/h. The heat flux was obtained from the temperature difference between the reaction channel inlet and outlet. Therewith, the heat flow $Q$ of each fluid flow can be calculated with

**Figure 5-18:** (a) The flow distribution in the cooling structure is illustrated in a detailed view. (b) Shows the stepwise invading fluorescein with 200 ml/h and (b) shows the flow distribution for 400 ml/h at two time steps with 1 s delay. The green shaded area depicts the microchannels filled with fluorescein.

**Heat conduction**

The cooling efficiency of the active heat sink in the microreactor was determined with a simple measurement setup. The silicon microreactor substrates were bonded and sealed with the in-channel electroless plating and contacted with affixed conventional tubings. Afterwards, the whole microreactor was encapsulated with a 2 mm thick layer of thermally insulating epoxy (*Endfest 3000*, Uhu, Germany). Furthermore, the whole chip was embedded in a thermally insulating polystyrene box. Two syringe pumps (*Injectomat 2000*, Fresenius, Germany) were connected to the test chip to feed the heating and cooling liquids. At the inlets and outlets, the temperatures of the liquids were measured with thermo elements (*Type T*, Labfacility, UK). The thermo elements were connected to a voltmeter (*NI 9219*, National Instruments, USA), and analyzed using a programmed virtual instrument (*Lab-View*, National Instruments, USA). The temperatures were determined with a mean temperature value taken from 100 measurements during 100 s. The thermal setup is schematically shown in Figure 5-19.

For the thermal measurements, the reaction microchannel was fed with 70 °C hot water and the cooling channels with 28 °C cold water. Highly demanding cooling situations, like in a microreactor, are typically managed with water instead of air or fluorochemical liquids as a coolant [10, 37]. The heated flow rate was fixed at 100 ml/h and 200 ml/h and the cooling flow rate was varied between 10 ml/h and 1000 ml/h. The heat flux was obtained from the temperature difference between the reaction channel inlet and outlet. Therewith, the heat flow $Q$ of each fluid flow can be calculated with
5.4 Functionality tests

\begin{equation}
\dot{Q} = \dot{M} \cdot c_p \cdot \Delta T \tag{5.11}
\end{equation}

where \( \dot{M} \) is the fluid mass flow in the channels, \( c_p \) the specific heat capacity of the fluids and \( \Delta T \) the temperature difference between inlet and outlet of the respective fluidic system. The results of the measurements are shown in Figure 5-20. The graph shows the heat flux out of the reaction channel for 100 ml/h and 200 ml/h liquid flow rate. The hot water is 70 °C and is cooled with 28 °C cool water in the active heat sink. The cooling flow is varied between 10 ml/h and 1000 ml/h. The dotted lines mark the maximum heat that is induced into the microreactor system: 4.8 W and 9.9 W for 100 ml/h and 200 ml/h heating flow, respectively.
heat flux of the heating flow rates of 100 ml/h (hf100) and 200 ml/h (hf200) as a function of the cooling flow rate. The heat flux increased for both heat flow rates rapidly at the beginning and saturated to the asymptotic maximum heat that was induced by the heating flow in the reaction channel (input: 4.8 W for 100 ml/h and 9.9 W for 200 ml/h). At a cooling flow rate of 400 ml/h already 76% (4.1 W) of the maximum heat for hf200 and 85% (7.6 W) of the maximum heat for hf100 were dissipated. At the maximum cooling flow of 1000 ml/h already 88% (8.7 W) for hf200 and 91% (4.3 W) for hf100 were dissipated.

From the temperature measurements of the cooling flow, the temperature increase was \( \Delta T_{\text{cool}} = 8.7 \) K that is assumed as the temperature increase of the whole microreactor. To proof the thermal model of the whole microreactor of subchapter 5.2.3 the temperature increase of the microreactor is calculated with hf100 and a cooling flow of 400 ml/h. This is equivalent to a heat flux of \( \dot{Q} = 4.1 \) W and a total thermal resistance of \( R_{\text{tot}} = 2.3 \) K/W. Therewith, results the temperature increase to \( \Delta T_{\text{sum}} = 9.4 \) K, see Eq (5.9). This is in the same order like the measured temperature increase \( \Delta T_{\text{cool}} \) and shows that the calculations give a reliable impression of the performance of the active heat sink. The same thermal model was also used to predict in worst case the maximum heat (\( \Delta T_{\text{reac}} = 16.38 \) K) at a thermal hot spot due to the fast reaction. This heating is tolerable for the chemical reaction and can be compensated with a cooling flow at lower temperatures.

### 5.4.3 Electroless plating of the microreactor structures

The most important step for the microreactor fabrication is the nickel plating of the microchannels and in particular the KOH nozzle. The function of the nickel layer is to seal the microstructured silicon substrate gas-tight against the highly corrosive fluorine gas. However, the metal plating can have small defects at edges and corners of the microchannel with high aspect ratios [32]. Through this defects, fluorine gas can penetrate the underlying substrate and start to etch the silicon. The metal plating is an electroless plating within the microchannel, as described in subchapter 3.3 and subchapter 5.3. The electroless plated nickel layers were tested for the chemical resistivity against fluorine and for a sufficient covering of the underlying silicon substrate, see subchapter 3.2. Additionally, the nickel layers in the microreactor were examined at the critical areas. Figure 5-21 shows a polished cross section of the microreactor with the reaction microchannel of 300 \( \mu \text{m} \times 300 \mu \text{m} \) and the 20 \( \mu \text{m} \times 80 \mu \text{m} \) KOH nozzle. The nickel layer was uniformly deposited on every channel wall with an approximate thickness of 30 \( \mu \text{m} \) to 40 \( \mu \text{m} \). The most crucial part for the in-channel plating is the nozzle orifice where the fluorine gas is injected into the liquid. The detailed view in Figure 5-21b shows a homogeneous and complete post-forming of the KOH nozzle with a 23 \( \mu \text{m} \) to 35 \( \mu \text{m} \) thick nickel layer. Therefore, the nozzle orifice has a length of 90 \( \mu \text{m} \). The different nickel layer thicknesses of the microchannel and the KOH nozzle indicate varying deposition rates between nozzle and microchannel. This fact has to be taken into account for the
5.4 Functionality tests

post-forming of the nozzle orifice to obtain the nominal opening size of 20 μm × 80 μm. The silicon substrate of a fabricated microreactor was etched away to release parts of the post-formed reaction microchannel and the nozzle. The procedure for the silicon etching is described in subchapter 3.3. The free etched reaction microchannel with the meander section is depicted in Figure 5-22a. An inspection of the released nickel micropipes showed that the whole silicon microchannel was completely post-formed without defects. Figure 5-22b shows a freestanding reaction microchannel. The nozzle was removed to examine the size of the orifice. The orifice was precisely post-formed and had a size of approximately 90 μm × 30 μm as already shown in the cross sectional view in Figure 5-21b. The post-formed pyramid-shaped nozzle made of electroless plated nickel that was removed from the reaction microchannel is shown in Figure 5-22c. This picture shows the exact post-forming of the KOH nozzle and the orifice. The metal structure at the pyramid bottom resulted from the fluidic contact between silicon and reactor platform. This nickel layer was quadratically lasered for the KOH etching step. The picture of the post-formed KOH nozzle shows impressively the possibilities of the in-channel electroless plating concerning precision, geometry, and stability.

Pressure tests

For a first test to detect possible defects in the nickel layer, released reaction microchannels were used. These freestanding microchannel with the surrounding chip frame are shown in Figure 5-22a, b. The micropipes were filled with fluorescein and

![Figure 5-21](image-url)
5 Microreactor

connected to a pressure supply at the chip frame. The microfluidic test chip was immersed in water to detect evading fluorescein and pressurized for 12 h up to 6 bar. No pressure loss and no fluorescein in the water was detected over this time. This means, that the micropipes are gas tight under pressure up to 6 bar. Hence, for the use in the microreactor, no fluorine gas should be able to penetrate the underlying silicon.

5.4.4 Chemical reaction

The microreactor system showed in the end of the first project part still some problems with the fluidic contact platform. For safety reasons, no direct fluorination reactions were

**Figure 5-22:** This figure shows released metal structures of the microreactor. (a) Shows the free etched meander part of the reaction microchannel. The silicon is completely etched and only the nickel channel and the palladium seed layer remain. (b) The reaction microchannel is completely released. The truncated pyramid-shaped nozzle was removed to expose the nozzle orifice in the microchannel wall. (c) Shows a detailed view of the truncated pyramid-shaped nozzle made of electroless plated nickel. The nozzle is released from the silicon substrate and the nickel microchannel.
performed in a microreactor. It was possible to fabricate the silicon microreactor with the needed accuracy and gas-tightness. However, the platform showed unexpected problems with the gas-tight sealing. It was not possible to seal the fluidic plate gas-tight to the fluidic connection plate, see Figure 5-15. The reason therefore was an insufficient smoothness of the copper plates. With that, in comparison to the silicon substrates, rough surface the in-channel electolless plating can not bridge the gaps between the two plates for sealing. This problem can be solved with pinch seals that are milled into the platform plates. Therefore, the platforms have to be thicker and larger to be able to apply the needed pressure to the pinch seal without deforming. Alternatively, the fluidic contacting in the chemical lab can be realized with a combined soldering and electolless plating of small nickel or Monel tubes without a fluidic platform. These possible solutions are part of the ongoing research within the working group.

5.5 Conclusion

This chapter has treated the design and fabrication of the silicon based microreactor and the reactor platform made of copper. The microreactor consists of three main units: the nozzle for the gas injection, the reaction channel, and the active heat sink. All fluidic units were covered with a nickel metal layer to seal the microstructured silicon substrate and the copper platform gas-tight against the highly corrosive fluorine gas.

The nozzle design uses the results of the bubble generation tests that were presented in chapter 2. The 20 μm × 80 μm KOH nozzle was used, because it is able to generate small and monodisperse microbubbles over a broad range of gas and liquid volume flow rates. The performance of the nickel coated microreactor nozzle was tested and showed only 7% difference of the generated bubble size to the silicon test nozzle. This difference was caused by size variations of the nozzle orifice due to fabrication.

For the design of the reaction microchannel a numerical study was performed to define the most effective meander structure with high Nusselt numbers (i.e. high heat flux) and the best mixing performance combined with the lowest pressure loss. The study compared meander, square wave, zigzag and optimized zigzag channel structures. The optimized zigzag showed the maximal heat transition ($N_u = 13.6$). Moreover, the mixing efficiency ($\alpha_V = 0.39$), the wall contact efficiency ($WE = 31.0 \times 10^{-3}$), and the pressure loss ($\Delta p = 796$ Pa) are comparable to the respective best meanders without the disadvantage of large dead zones. Furthermore, the transient simulation have shown that the optimized zigzag had a high convection around the injected bubbles. That proved that the optimized zigzag is the best meander structure in the microreactor for the direct fluorination. The optimized zigzag channel design for the microreactor is, therefore, a zigzag structure with a 60° angle. The apex is rounded with a widening of the channel width and the straight channel parts have a taper of the channel width for an optimized fluid flow with reduced dead zones.

The generated heat in the microreactor is removed by an integrated micro heat sink that
consists of an array of parallel microchannels. A constant water stream flows through these channels and absorbs the heat flux provided by the reaction channel. For this design the heat transfer was calculated for the worst case during the aimed toluene fluorination at room temperature (30 ml/h F₂ with 70 ml/h toluene). The calculation showed only a heating of $\Delta T_{sum} = 0.39 \text{ K}$ for the whole microreactor and a maximum heating of $\Delta T_{reac} = 16.38 \text{ K}$ for a minimal area hot spot. Additionally to the calculations the heat sink efficiency was measured with a test setup. These measurements of the microreactor demonstrated heat transfer values that were comparable to the calculations. Hence, the measured temperature increase was with $\Delta T_{cool} = 8.7 \text{ K}$ in the same range as the calculated temperature increase for the test setup of $\Delta T_{sum} = 9.4 \text{ K}$.

Electroplating and electroless plating of nickel were used to encapsulate the silicon microreactor and to integrate it into the reactor platform. This fabrication method was analyzed for homogeneous plating in the complex fluidic structures. Furthermore, the structures were tested for gas tightness to ensure an efficient protection of the underlying silicon against the aggressive fluorine gas. The nickel layers showed no defects and were gas tight up to 6 bar.

With all these combined units a complete microreactor was fabricated that performs the challenging demands of direct fluorination: (a) Injection of small monodisperse microbubbles for a large interfacial area. (b) An optimized mixing in the reaction microchannel to accelerate the chemical reaction and enhance the heat flux out of the reaction substrate. (c) This heat flux has to be effectively dissipated by the active heat sink to avoid local hot spots. (d) Moreover, all these fluidic units have to be covered gas tight with a nickel layer against the highly aggressive fluorine gas.

This facilitates, in principle, the first direct fluorination reactions with the microreactor as the next step of the project. This experiment is currently in process. Therefore, the task of the gas-tight fluidic contact platform has to be solved.
5.6 References


5.6 References


6 Further applications for in-channel electroless plating

6.1 Introduction

The fabrication method to postform microfluidic channels with the in-channel electroless plating is described in subchapter 3.3 and [1, 2]. This novel technique provides a gas-tight and chemically resistant sealing of the silicon substrate with nickel for the direct fluorination microreactor pursued here. Moreover, metal micropipes can be fabricated in three dimensions (3D) and it is possible to release these micropipes from the surrounding silicon chip with potassium hydroxide etching (KOH). For the microreactor application, this was used to test the homogeneous metal deposition for material strength and gas-tightness. Beyond the described microreactor application, this fabrication method enables numerous applications for microfluidic and microreaction applications.

Microfluidic mixing devices in 3D show enhanced mixing qualities compared to two dimensional (2D) devices [3, 4]. Furthermore, 3D microchannels allow the design of complex structures and intersecting routes of the microchannels. This enables an integration of fluidic structures on smaller spaces. Partially released walls of the metal micropipes function as membranes that can be used as temperature or pressure sensors. On the other hand, an actuated membrane can be used for pumping, mixing or venting purposes. With micropipes completely released from the substrate, it is possible to decouple parts of the microchannel thermally on a single chip. This is a benefit for a rapid quenching or heating of chemical reactions such as partial oxidations [5] or in micro total analysis systems (μTAS) with reactions like the polymerase chain reaction (PCR) [6]. The released micropipes provide the opportunity to locate them directly within the cooling liquid similar to conventional tube bundle heat exchangers. Therewith, the conductive heat resistance in the wall is insignificant and the heat flux density depends only on the liquid flows. Furthermore, freestanding micropipes allow deflection and oscillation, which can be used either for active mixing purposes or for coriolis mass flow sensors. These mass flow sensors were already used in micro dimensions with silicon oxide channels presented by Enoksson et al. [7] and Sparks et al. [8]. All these suggested applications are only a brief summary of the opportunities available due to this novel fabrication technique.

During this thesis, two applications were investigated in-depth to confirm their advantage over comparable devices. This chapter describes the advantages of 3D compared to 2D mixing microchannels with fluorescein experiments. In addition, the heat conduction characteristics for embedded and freestanding micropipes were determined theoretically and experimentally with a cross-flowing coolant liquid in silicon test chips.
6.2 Improved mixing in 3D microchannels

The mixing performance in microchannels essentially increases with 3D instead of 2D structures in normally used microfluidic devices [3, 4]. Nevertheless, only the group of R.H. Liu et al. [3] worked with 3D structured meander microchannels and showed that these structures induce chaotic advection and enhance the fluid mixing. This effect is dominant at low Reynolds numbers ($Re < 200$) and was numerically verified by Y.Z. Liu et al. [9]. This work uses the design proposed by Ottino [10]. In this design, chaotic advection is produced with bends in the microchannel that induce a secondary Dean flow, whereby the Dean vortices are rotated by 90° in each bend, see also subchapter 5.2.2 and the thesis of Dreher [14]. This chapter discusses the enhanced mixing performance of a simple 3D mixing microchannel, produced with the in-channel electroless plating, compared to a 2D equivalent. For further details of the experiments see the master’s thesis of Neiss [11].

6.2.1 Fluidic chip

The microfluidic test chips were fabricated according to the in-channel electroless plating technique, that is described in subchapter 3.3. The postformed nickel microchannels were not released from the silicon substrate. The top substrate is made of transparent pyrex glass to enable an optical observation of the mixing performance. Figure 6-1 shows scaled drawings of the used silicon chip designs with the 2D and 3D mixing microchannels from the top. All microchannels had a nickel wall thickness of 30 μm and

![Figure 6-1: Drawing of the silicon test chips for the measurements of the mixing performance for mixing in (a) 2D and (b) 3D microchannels.](image)
6 Further applications for in-channel electroless plating

a cross section of 240 μm × 240 μm. The chips had two inlets (in1, in2) and one outlet. The two inlet channels merge at a Y-junction. These junctions were 2.5 mm upstream of the first bend of the mixing device for both designs. The design of the 2D chip required only one bottom layer for the channels, whereas the chip with the 3D mixing channel needed an additional top layer for the outlet channel after the mixing device with the upward bend. Figure 6-2a shows schematically a silicon test chip with liquid channels and the pyrex cover on top for optical observation of the mixing devices. The 2D and 3D mixing devices were microchannels with three bends and characteristic channel lengths of 400 μm after the first bend and 225 μm after the second bend. Both variations were identical except the direction of the second bend that determined the dimension for the 2D or 3D mixer. The sketches with the characteristic lengths and pictures of the mixing devices are shown in Figure 6-2b for 2D and Figure 6-2c for 3D. These simple mixing structures allow to determine the difference in design and mixing quality between 2D and 3D mixers.

6.2.2 Setup

The measurement setup to determine the mixing quality is schematically shown in Figure 6-3. Flow tests with fluorescein were performed to analyze the mixing qualities in 2D and 3D microchannels. For these experiments, the characterization of the mixing quality was performed with two liquids. One liquid was an aqueous, quenched fluorescein solution (acid) and the other liquid was an aqueous, alkaline sodium hydroxide solution.

![Figure 6-2](image)

Figure 6-2: (a) Schematic view of the microfluidic test chip with two inlets (in1, in2) and an outlet. The pyrex cover allows an optical observation of the mixing. These mixing devices are shown in sketches and photographs for (a) the 2D mixing channel and (b) the 3D mixing channel. The shaded area in the sketches indicates the area covered with pyrex glass.

6.2.2.2 Setup

The measurement setup to determine the mixing quality is schematically shown in Figure 6-3. Flow tests with fluorescein were performed to analyze the mixing qualities in 2D and 3D microchannels. For these experiments, the characterization of the mixing quality was performed with two liquids. One liquid was an aqueous, quenched fluorescein solution (acid) and the other liquid was an aqueous, alkaline sodium hydroxide solution.
6.2 Improved mixing in 3D microchannels

During mixing of these two liquids, the quenching was neutralized and fluorescence light was emitted. Due to the mixing, concurrently the concentration of the fluorescein tracer was reduced. With an optimized adjustment of these two factors the maximum of the emitted light was equivalent to the maximum of the mixing quality.

The setup consists of the microfluidic chip mounted in a fluidic carrier (see subchapter 2.5.2) and two syringe pumps (Injectomat 2000, Fresenius, Germany) that fed the liquids of fluorescein as tracer and the diluting agent of sodium hydroxide. A switching device allowed to switch the solvents between the two inlets of the chip (in1, in2). The liquids of the two microchannels merged in a Y-formed junction to prevent mixing of the liquids upstream the mixing device. The mixing device was observed through a microscope (BX51, Olympus, Japan) with the filter set XF100-3 (Melles Griot, USA). Only wavelengths of the light source lower than 500 nm passed the excitation filter while the emission filter passed only light with wavelengths higher than 500 nm. Fluorescein has the absorption maximum at 489 nm and emission maximum at 516 nm for the used solution. Thus, only emitted light of fluorescein was detected with the microscope. For details of fluorescein and the according test setups, please refer to the work of Diehl et al. [12]. The fluorescein distribution in the mixing device was evaluated qualitatively with a camera (EOS 500D, Canon, Japan) or quantitatively with a light sensitive photodiode setup. This setup was a photodiode (BPW 21, Siemens, Germany) with a transimpedance amplifier whose output voltage increased linearly with the light intensity. The photodiode amplifier contains an operational amplifier (LMC6482, National Semiconductor, USA) with a 10 GΩ feedback resistor and operates with a supply voltage of $U_{ss} = 15$ V. The mains hum was canceled by a passive low pass filter with the cutoff frequency of 7.5 Hz. The circuit diagram is displayed in Figure 6-4.
6 Further applications for in-channel electroless plating

The photocurrent $i_P$ depends on the illumination intensity $E$ and the photosensitivity ($10 \text{ nA/lx}$) of the photodiode amplifier. Hence, the voltage output $V_{\text{out}}$ can be calculated with

$$V_{\text{out}} = 10 \text{ G}\Omega \cdot i_P = 10 \text{ G}\Omega \cdot 10 \text{ nA/lx} \cdot E$$

(6.1)

and correlates linearly to the light intensity. This voltage is normalized to the maximal possible voltage $V_{\text{max}}$ for every specific measurement to cancel the influence of the spectral photosensitivity. That implies the fluorescence intensity to be normalized to the maximal possible intensity $E_{\text{max}}$:

$$\frac{V_{\text{out}}}{V_{\text{max}}} = \frac{10 \text{ G}\Omega \cdot 10 \text{ nA/lx} \cdot E}{10 \text{ G}\Omega \cdot 10 \text{ nA/lx} \cdot E_{\text{max}}} = \frac{E}{E_{\text{max}}},$$

(6.2)

Figure 6-5 shows a picture of the complete setup for the fluorescence measurement of the mixing performance.

**6.2.3 Theoretical background**

**Mixing performance**

Mixing performance of a microchannel can be quantified by a volume flow based mixing quality like for the simulations in subchapter 5.2.2 [see Eq (5.1) and Eq (5.2)]. This value is an efficient indicator for dynamic processes but it requires a big effort for measurements with particle image velocimetry (PIV). However, the mixing quality can also be analyzed with a statistical approach of Bothe et al. [13]. The volume based mixing quality is

$$\alpha_V = 1 - \frac{ad}{ad_{\text{max}}} \text{ with } ad = \int_{V_{\text{tot}}}^{V_{\text{tot}}} \left(\epsilon - \bar{\epsilon}_V\right)^2 dV,$$

(6.3)

where $V_{\text{tot}}$ is the observed channel volume with the concentration $\epsilon$. The concentrations
6.2 Improved mixing in 3D microchannels

$c = 1$ and $c = 0$ indicate fluid with and without fluorescein tracer, respectively. A mixture of equal parts from both fluids has $c = 0.5$. Measurements with this distribution need a stable volume flow rate which was not achievable with the used syringe pumps at low flow rates. To avoid this problem, the absolute average deviation 

$$aad = \frac{1}{V_{tot}} \int_{V_{tot}} \sqrt{(c-V)^2} dV,$$  \hspace{1cm} (6.4)

is used instead of the standard deviation for the modified mixing quality:

$$\alpha_V^* = 1 - \frac{aad}{aad_{max}} \text{ with } aad_{max} = 2 \cdot \bar{c} \cdot (1 - \bar{c}).$$  \hspace{1cm} (6.5)

The advantage of this approach is the freedom to choose the reference concentration $\bar{c}_V$ and, therewith, the ratio of the volume flow rates as reference of the fully mixed state.

Fluorescein mixing

Fluorescein (Fl) was used experimentally to characterize the mixing quality of two liquids within the mixing channels. One feed stream has a maximum concentration of Fl tracer $c = 1$ (acid) and the second has no tracer $c = 0$ (base). Mixing of both liquids varies the concentration, which is calculated with the volume fraction $\varphi_{base}$ of the base ($V_{base}$) and the acid ($V_{acid}$):

![Figure 6-5: This picture shows the setup for the mixing measurements in 2D and 3D microchannels with.](image)
Further applications for in-channel electroless plating

The Fl concentration of the mixture decreases linearly with an increasing amount of base. Hence, the fluorescence intensity \( E \) normalized to the maximum intensity \( E_{\text{max}} \) is given by

\[
\frac{E}{E_{\text{max}}} = 1 - \varphi_{\text{base}},
\]

when the Fl concentration does not exceed the saturation concentration.

For Fl measurements not only the concentration but also the pH value of the mixed liquids influence the fluorescence intensity of the emitted light. Therefore, the pH values have to be set carefully for the base and the acid. The pH values were set for the quantitative measurements at pH = 4 for the acid (Fl concentration of 0.05 g/l) and pH = 10.5 for the base. Within this pH range it was possible to receive a reliable, overall intensity plot for different volume fractions of the base, see Figure 6-6. The graph also shows the theoretical behavior of the intensity that depends on the concentration and the pH value. The formula of the theoretical approach is based on the work of Diehl et al. \[12\] and combines the concentration and pH value dependency of the fluorescence intensity. For further details please refer to the appendix in subchapter \[1\] and the master’s thesis of Neiss \[11\]. The measured values correlate with the theoretical behavior of the mixed solutions. The maximum intensity in Figure 6-6 and, hence, the mixing optimum of the theoretical and measured values in this plot is at \( \varphi_{\text{base}} = 0.45 \). Furthermore, the intensity curve is not symmetrical to the maximum intensity.

The fully mixed state of the two liquids should be at \( \varphi_{\text{base}} = 0.5 \) with a symmetrical curve progression. Therewith, the mixing quality can be determined. The best mixing quality is indicated by the highest intensity and decreases symmetrically with increasing and accordingly decreasing saturation concentration \( \varphi_{\text{base}} \). This can be achieved by two equivalent measurements with switched inlets. This mirrors the function derived for the fluorescence intensity of Figure 6-6 at \( \varphi_{\text{base}} = 0.5 \). For an arbitrary mixing element, the average of both measurements leads to a base-to-intensity distribution that is shown in Figure 6-7. The analytical curve for the base-to-intensity distribution can be approximated by

\[
\frac{E}{E_{\text{max}}} = 1 - 2 \cdot \| \varphi_{\text{base}} - 0.5 \| = 1 - 2 \cdot \sqrt{\left( \varphi_{\text{base}} - 0.5 \right)^2}.
\]
Figure 6-6: This graph shows the measured fluorescence intensity for different mixed saturation concentrations $\phi_{\text{base}}$ of the base solution (pH = 10.5) with the acid fluorescein solution (pH = 4). These values correlate with the theoretical behavior of the mixed solutions.

Figure 6-7: This plot displays the theoretical and approximated base-to-intensity distribution for an intensity measurement of an arbitrary mixing element with switched inlets. The switching mirrors the curve at $\phi_{\text{base}} = 0.5$. The pH values for the base is pH = 10.5 and for the acid pH = 4.
Further applications for in-channel electroless plating

With the assumption that the tracer concentration is equal to the amount of acid (Fl solution), the volume fraction \( \phi_{\text{base}} \) can be replaced by \( (1 - \epsilon) \). For equal volume flow rates of both feed streams (base and acid), the average volume flow based tracer concentration is \( \epsilon = 0.5 \). Thus the mean intensity over a defined volume of Eq (6.9) matches the modified mixing quality \( \alpha^*_V \) of Eq (6.5). From these two equations follows

\[
\frac{E}{E_{\text{max}}} = \frac{1}{V_{\text{tot}}} \int \frac{1 - 2 \cdot \sqrt{(\phi_{\text{base}} - 0.5)^2}}{V_{\text{tot}}} \, dV
\]

\[
= 1 - \frac{2}{V_{\text{tot}}} \int \sqrt{(\phi_{\text{base}} - 0.5)^2} \, dV.
\]  

(6.9)

With the assumption that the tracer concentration is equal to the amount of acid (Fl solution), the volume fraction \( \phi_{\text{base}} \) can be replaced by \( (1 - \epsilon) \). For equal volume flow rates of both feed streams (base and acid), the average volume flow based tracer concentration is \( \epsilon = 0.5 \). Thus the mean intensity over a defined volume of Eq (6.9) matches the modified mixing quality \( \alpha^*_V \) of Eq (6.5). From these two equations follows

\[
\alpha^*_V = 1 - \frac{aad}{aad_{\text{max}}} = 1 - \frac{\frac{1 - E/E_{\text{max}}}{2}}{0.5} = \frac{E}{E_{\text{max}}},
\]  

(6.10)

with a maximal average deviation of \( aad_{\text{max}} = 0.5 \) at a continuous mixing process with equal flow rates.

This measurement principle with fluorescein enables a simple detection of a mixing quality in a given liquid volume, but there are still some problems associated with the small deviations between theoretical and approximated curve in Figure 6-7 and the pH value accuracy of the solutions. However, these inaccuracies induce a maximum error of 5.3%, for further details of the error analysis see [11]. Thus, the presented fluorescein model can be used to analyze quantitatively the mixing performance of 2D and 3D mixing microchannels with sufficient accuracy.

### 6.2.4 Measurements and discussion

The 2D and 3D mixing devices were compared qualitatively with fluorescein as active tracer to determine the mixing quality \( \alpha^*_V \). One liquid contained the tracer (acid) and one liquid was without tracer (base). The acid solution was prepared with hydrochloric acid (HCl) and deionized (DI) water. An amount of 0.05 g/l fluorescein-sodium was dissolved in the solution to pH = 4.0. The base solution was prepared only with sodium hydroxide (NaOH) and DI-water to pH = 10.5.

The pictures in Figure 6-8 illustrate the mixing performance for 2D and 3D at Re = 150. Bright areas in the pictures indicate a high mixing quality. Following this criterium, the 3D mixer in Figure 6-8b showed a better mixing quality. The evaluated volume to determine quantitatively the mixing performance with the photodiode setup were quadratically and had side lengths of 240 \( \mu \)m. The position of the volumes were 715 \( \mu \)m downstream, related to the edge of the last bend of the mixing device. This is shown in Figure 6-8 for the 2D and the 3D mixer.

Three separate measurements were necessary to calculate the mixing quality \( \alpha^*_V \) from the
6.2 Improved mixing in 3D microchannels

The emitted fluorescence intensity within the evaluated volume. First, the maximum intensity $E_{\text{max}}$ was measured with a mixed solution of 50% base and 50% acid, representing a mixing quality $\beta_V = 1$. Second, the acid solution was injected into one inlet while the base solution was injected into other inlet and the intensity was measured ($E_a$). Third, this measurement was repeated with switched inlets ($E_b$), and both intensity values were normalized to the measured intensity of the perfect mixture. The mixing quality $\beta_V$ is the average of these two values:

$$\beta_V = \frac{E_a + E_b}{2 \cdot E_{\text{max}}}.$$  \hspace{1cm} (6.11)

The results of the quantitative measurements are shown in Figure 6-9. The mixing qualities of the 2D and 3D mixing devices were determined for different Reynolds numbers between Re = 43 and Re = 150. The indicated error bars represent the difference

---

**Figure 6-8:** This picture shows the flow structure visualized with fluorescein at a Reynolds number of Re = 150 for (a) the 2D microchannel mixer and (b) the 3D microchannel mixer. The evaluated volume is used for the quantitative mixing quality analysis and its position is related to the edge of the last bend.
of the two necessary measurements and the oscillation of the syringe pump. Both mixers showed slightly increasing mixing qualities with increasing Reynolds numbers. The 2D mixer increases the mixing quality from $\alpha^*_V = 0.229$ at $\text{Re} = 43$ to $\alpha^*_V = 0.31$ at $\text{Re} = 150$. In comparison, the mixing quality of the 3D mixer increased from $\alpha^*_V = 0.34$ at $\text{Re} = 43$ to $\alpha^*_V = 0.47$ at $\text{Re} = 150$. This shows that the 3D mixer has constantly better mixing qualities with a factor between 1.5 and 1.7 within the measured Reynolds numbers.

The advantages of 3D micro mixers were analyzed with a simple measurement setup that allows fast and easy-to-handle measurements. The mixing performance of the 2D and the 3D mixing devices showed a distinctive benefit of mixing structures with three dimensions for low Reynolds numbers. This is an important benefit for fast chemical reactions in microreactors.

The influence of the microchannel dimensions and the characteristic length between the bends of the microchannels were not analyzed yet, but will be shown as next step of the project [11]. Moreover, the mixing performance was measured only for one sequence of the mixing device to allow the detection of distinguishable differences in light intensity. Larger 3D mixing devices with repeating bends and loops should increase the mixing performance decisively, but this has to be analyzed in-depth by further experiments and simulations.

Figure 6-9: This graph shows the mixing quality for the 2D and the 3D mixing microchannels at different Reynolds numbers between $\text{Re} = 43$ and $\text{Re} = 150$. 
6.3 Heat transfer of freestanding metal micropipes

Besides the mechanical properties and the chemical resistivity of the freestanding micropipes, the improved heat dissipation out of the micropipe into a surrounding cooling liquid is a great benefit for microreaction engineering. To show the advantages of a freestanding micropipe compared to an embedded micropipe a simple test setup with 2D micropipes was used. The fabrication of the chip is equivalent to the fabrication method in subchapter 3.3. For further details of the experiments see the bachelor thesis of Wiedenmann [15]. These 2D, u-shaped micropipes are shown in Figure 6-10.

Figure 6-10: Silicon microchip with released 2D nickel micropipes. The channels are 300 μm wide and 150 μm high with a wall thickness of 20 μm.

6.3.1 Setup

Figure 6-11 shows a scaled drawing of the used silicon chip with the 2D, u-shaped micropipes. All micropipes had a nickel wall thickness of 20 μm. They were 300 μm wide and the height was 150 μm. The cooling chamber had a cross section of 8 mm × 8 mm and was fed by fluid channels of the same size as the micropipes. The chamber was 525 μm deep for the embedded chip and 1050 μm deep for the released chip. A part of the u-shaped pipe was within the cooling chamber area with a total length of 7.5 mm.

The thermal test setup with the 2D microchannel is schematically shown in Figure 6-12. This test chip had two fluidic systems for heating and cooling, respectively. Hot water was pumped through the metal micropipe and cool water was pumped through the cooling chamber around the u-shaped micropipe (see Figure 6-12a). The temperature difference between the fluid inlets and outlets was determined with four measurement points at the inlet and outlet of both fluidic systems, respectively. For a simplified model the overall thermal flow $Q$ out of the heated microchannel can be subdivided into three thermal flows, $Q_1$ in the first part of the silicon frame, $Q_2$ from the metal pipe into the cooling liquid, and $Q_3$ in the second part of the silicon frame as indicated in Figure 6-12a. The
cross sections in Figure 6-12b show the different test models. The test chip named model A is a metal micropipe embedded in silicon. The area above the micropipe was cooled via a structured silicon layer with a pyrex glass cover on top. These glass chips were simply placed on the silicon chips without bonding because the pressure of the chip carrier fixes them sufficiently. The same cooling area was opened and releases the metal microchannel for the test chip model B. This means that the cooling liquid was able to flow around the micropipe. The opened area with the freestanding pipes was covered with pyrex glass like at model A. The glass of both models allowed an optical observation and works also as a thermally insulating layer.

The test setup for the temperature measurements is shown in Figure 6-13. The fluidic test chip was mounted in a chip carrier with fluid connectors, see subchapter 2.5 and [14]. Syringe pumps (*Injectomat 2000*, Fresenius, Germany) were connected to the test chip to feed the heating and cooling liquids. The initial heating temperature was 55 °C and the initial cooling temperature was set at room temperature (25 °C). The temperatures were detected with thermo elements at the fluid inlets and outlets (*Type T*, Labfacility, UK), connected to a voltmeter (*NI 9219*, National Instruments, USA), and analyzed using a programmed virtual instrument (*Lab-View*, National Instruments, USA). The temperatures are determined with a mean temperature value taken from 100 measurements during 100 s.

**Figure 6-11:** Drawing of the silicon test chip for the heat conduction tests with embedded and released 2D micropipes.
6.3 Heat transfer of freestanding metal micropipes

Figure 6-12: (a) This sketch shows a top view of the silicon test chip with the u-shaped channel for the heat flow and the chamber opening for the cooling flow. The temperatures are measured at the inlets and outlets of the fluid systems. (b) Cross sectional view of the embedded model A and the released model B with the indicated heat flow $\dot{Q}_2$ out of the channel into the cooling liquid.

Figure 6-13: This picture shows the experimental setup with the microfluidic test chip (model B) mounted inside the chip carrier. The chip carrier is connected to the heating and cooling liquid supply. The temperatures of the liquids upstream and downstream of the chip are measured with thermo elements.
6.3.2 Thermal model

According to the first law of thermodynamics the heat flow $\dot{Q}$ out of a fluid channel is defined as [16]

$$\dot{Q} = \dot{M} \cdot c_p \cdot \Delta T$$  \hspace{1cm} (6.12)

with the fluid mass flow $\dot{M}$ in the channel, the specific heat capacity $c_p$ of the fluid and the temperature difference $\Delta T$ between inlet and outlet of the system. The heat flow

$$\dot{Q} = \frac{\Delta T}{R_{th}}$$  \hspace{1cm} (6.13)

can also calculated with the thermal resistance $R_{th}$ and the temperature difference $\Delta T$. The difference of the two chip models, i.e. the embedded (A) and the released (B) micropipe, is represented by different thermal resistance models in Figure 6-14. Thermal resistances are analog to electric resistances and therefore treated in an analogon to Ohm’s law. In this application, two types of thermal resistances exist, the conduction and the convection resistances. Within a material, the conductive resistance

$$R_{\text{cond}} = \frac{l}{\lambda \cdot A}$$  \hspace{1cm} (6.14)

is across the length $l$ of the material with the thermal conductivity $\lambda$ and the cross sectional area $A$ of the conducting heat path. The convection resistance

$$R_{\text{conv}} = \frac{1}{\alpha \cdot A}$$  \hspace{1cm} (6.15)

describes the heat transfer by convection at a surface area $A$ with the convection heat

---

**Figure 6-14:** This schematic sketch shows the thermal resistance model for the embedded and released 2D micropipes. The resistance indices stand for the convective resistance from the heated water into the nickel channel wall ($H_2O$-Ni), from the nickel channel wall into the cooling water ($Ni$-$H_2O$) or from the silicon substrate into the cooling water ($Si$-$H_2O$). The conductive resistances are present in the nickel wall and in the silicon substrate ($Ni$, $Si$), respectively.
transfer coefficient $\alpha$. This heat transfer coefficient depends for fluids on the Nusselt number ($Nu$) and, as a consequence, on the Reynolds number ($Re$) [17]. The dimensions of the fluidic reference system are defined by the hydraulic diameter ($d_H$) [17].

The embedded model A has thermal resistances from the heated water into the nickel channel wall and within the nickel channel wall. This is continued by the resistance in the silicon substrate and from the substrate into the cooling liquid. The heat transition resistance between the nickel and the silicon layer can be neglected. The models show, that the embedded model A has one resistance more than the released model B. This is the conductive resistance of the silicon substrate. The total resistance of model A is higher than the total resistance of model B. Hence, with a constant temperature difference $\Delta T$ model B has a higher thermal flow $Q_2$ from the heating system to the cooling system. Furthermore, the significant difference of the thermal resistance models is the transition area $A$ of the convective resistance into the cooling water. For the embedded model A, the effective heat transition length of a 2D cross section was simulated with finite element simulation (FEM) in ANSYS 13 (ANSYS Inc, USA). The simulations were done with a hot microchannel (55°C) within a silicon substrate. The silicon channel is 300 μm wide and 150 μm high. The silicon substrate is 525 μm thick and the microchannel is positioned at the bottom side and in the middle of the 8 mm long substrate. This substrate has only one cool wall on the top, representing the cooling flow, for heat dissipation and all other walls were adiabatic. The effective length of heat dissipation on the silicon surface results due to the heat spreading within the solid silicon [19, 20]. In this application, the effective heat dissipation length is defined by the length with 95% of the total heat flux out of the silicon. The heat flux in silicon was simulated with different temperatures (28 °C, 33 °C, and 38 °C) of the cool surface to evaluate the mean transition length along the u-shaped channel. The three temperatures represent the temperature of the cooling liquid in best case if it is still cool and in worst case if the cooling liquid is already heated up. The simulation heat flux contour is displayed in Figure 6-15. The simulations show that the

![Figure 6-15: This picture shows the result of the thermal flux simulations. The microchannel has a temperature of 55 °C and the heat flows through the silicon substrate to the cool silicon surface of 28 °C. The effective heat transition length (2.16 mm) is defined as the length with 95% of the heat flux out of the silicon surface. Left and right edges cropped for illustrative purposes.](image-url)
heat transition length is 2.16 mm for all three simulated temperatures. A graph of the heat flux $\dot{Q}$ out of the cool surfaces is plotted in Figure 6-16. Along the u-shaped microchannel results, with this length, a heat transition area of 13.9 mm$^2$. The cooling liquid of the released model B flows directly around the micropipe and the transition area is the micropipe surface area of 7.2 mm$^2$. This results in a higher convectional resistance into the cooling liquid for model B but also a higher heat flux density $\dot{q}$ (W/mm$^2$) per time and area size.

**6.3.3 Measurements and discussion**

All temperature measurements were done with two different volume flows (40 ml/h, 60 ml/h) of the heating system through the metal micropipe and a volume flow variation of the cooling system between 4 ml/h and 16 ml/h. The measured temperature differences between the inlets and outlets and the used liquid volume flows allows to obtain the overall heat conduction $\dot{Q}$ of the chip, see Eq (6.12). To determine the thermal flow $\dot{Q}_1$ and $\dot{Q}_3$ of the chip frame, the cooling chamber is filled with air for both chip models. Air has a heat conduction of 0.03 W/(K m) [18]. This is a perfect thermal isolation compared to the thermal conduction of silicon [150 W/(K m)] or nickel [91 W/(K m)] of the surrounding chip frame [32]. With those measurements, the thermal flow within the footprint of the

![Figure 6-16](image_url)

**Figure 6-16:** This graph shows the heat flux out of the 8 mm long the silicon surface. The hot (55 °C) microchannel is positioned in the middle of the substrate length. The cool surface was simulated with three different temperatures: 28 °C, 33 °C, and 38 °C. The heat transitions length is 2.16 mm with 95% heat flux out of the surface.
cooling chamber $Q_2$ can be determined. Due to the small temperature differences of maximal 13 °C the temperature course from $Q_1$ to $Q_2$ and $Q_3$ is nearly linear. Hence, $Q_2$ can be calculated with:

$$Q_2 = \dot{Q} - \dot{Q}_1 - \dot{Q}_3.$$  \hfill (6.16)

To compensate the difference of the transition area into the cooling liquid, the heat conduction $Q_2$ is normalized as heat flux density $\dot{q}_2$ of the transition area of the different chip models, respectively. The results of the measurements are shown in Figure 6-17. The graph shows the heat flux densities of the different thermal models as a function of the cooling fluid flow rate.

The heat flux density for the embedded model A at a heating flow of 40 ml/h starts at a cooling flow rate of 4 ml/h with 4.6 mW/mm$^2$. With an increased cooling flow rate of 16 ml/h it increases only slightly to 11.1 mW/mm$^2$. The higher heating flow of 60 ml/h shows the same performance at higher levels with 14.7 mW/mm$^2$ at a cooling flow rate of 4 ml/h and 21.6 mW/mm$^2$ at 16 ml/h cooling flow rate. The observed setoff occurs due to higher flow rates of the heating liquid and therefore a lower heat transfer coefficient $\alpha$. Compared to the embedded model A, the released model B shows higher heat fluxes and responds much better to the cooling flow rate variation. At a heating flow rate of 40 ml/h,
the heat flux of model B increases from 1 mW/mm$^2$ to 14 mW/mm$^2$. Up to a cooling flow rate of 8 ml/h the heat flow density is smaller than in model A but with increasing cooling flow rate model B shows higher heat flux densities. The difference to model A and the influence of the direct cooling flow around the micropipe is impressively shown with the heat flux at a heating flow rate of 60 ml/h. The heat flux increases from 15 mW/mm$^2$ at 4 ml/h to 40.5 mW/mm$^2$ at 16 ml/h cooling flow rate. This is a 2.7 times increase of the heat flux density compared to the relatively small 1.4 fold increase within the embedded model A.

The thermal measurements show that the released metal micropipes of model B allow to control the heat flux density very efficient only by changing the cooling flow rate without changing the temperature of the cooling fluid. Hence, the temperature in the heating pipe can be adjusted easily and fast by a variation of the cooling flow rate. Micro heat sinks have in general small channels to provide sufficiently large contact areas [21]. However, small channels induce high pressure loss which represents an effort for the applied fluid flow. Therefore, the ratio of heat transfer to pressure loss has to be taken into account [5]. The presented heat sink setup with the heated micropipe in a wide cooling chamber indicates a lower pressure loss for the cooling flow with higher heat fluxes, relatively to other microfluidic heat sinks.

### 6.4 Conclusion

In conclusion, two promising applications of the in-channel electroless plating technique are presented to produce freestanding 3D micropipes: first, the enhanced mixing performance of 3D mixing microchannels and, second, the improved cooling efficiency due to freestanding micropipes within the flowing cooling fluid.

Simple 2D and 3D mixing microchannels with three bends were produced with the in-channel electroless plating fabrication method. The mixing performance was analyzed with a simple and easy-to-handle fluorescein measurement setup. Emitted fluorescence light of the mixed liquids was detected with a transimpedanz photodiode setup. Therewith, it was possible to determine the mixing quality by the measured voltage due to the adapted mixing quality and fluorescein theory. Thus, the distinctive benefit of mixing structures with three dimensions for low Reynolds numbers was determined.

Thermal measurements had shown that released 2D micropipes provide better heat flux densities than embedded micropipes. Therewith, they allow an accurate control of the temperature in the micropipe only with a variance of the cooling fluid flow rate.

These two applications are an important benefit for fast and highly exotherm chemical reactions in microreactors, such as the direct fluorination of liquid solvents.
6.5 References


6 Further applications for in-channel electroless plating


6.5 References
7 Conclusion and outlook

This thesis describes the modeling, design and fabrication of microfluidic unit operations and specific microfabrication methods that enable a direct fluorination of liquid solvents in micro dimensions. Silicon-based microreactor systems for these reactions have to withstand the challenging demands of the harsh reaction conditions. The most significant demands of direct fluorination are the fast reaction rate that is basically limited by the interfacial area, the excessive heat generation, and the highly corrosive reaction environment due to the aggressive reagents fluorine and hydrogen fluorine.

7.1 Major outcomes

The main achievements of this work are the successful development of a micronozzle concept for monodisperse microbubble generation and a novel fabrication method for sealed metal micropipes. Compared to the state of the art microreactors for direct fluorination, the results of this thesis provide the following improvements:

• Monodisperse bubble generation with high frequencies (500 Hz - 1800 Hz), with bubbles smaller than the reaction microchannel width and, therewith, large interfacial areas for the fluorine reaction.
• Simple fabrication method for gas-tight and chemically resistant microfluidic metal structures.
• Efficient and sophisticated microfluidic components for mixing and cooling.
• Operation with higher throughput of 100 ml/h and higher fluorine concentrations up to 88% with a high conversion of 96%.
• Long term stability of the microreactor structures (100 h) due to the nickel plating fabrication.

These developments are the key aspects for silicon-based microreactors for direct fluorination. Thus, it was possible to design, fabricate and test all necessary units and fabrication methods for a complete microreactor system. The major outcomes of this thesis are described in the following.

Micronozzles were developed and verified for their application in the direct fluorination microreactor. The unique features of this micronozzle design are the generation of monodisperse microbubbles with a diameter of about 200 μm in the reaction microchannel with a cross section of 300 μm × 300 μm and a coating of the micronozzles with a chemically inert nickel layer. A theoretical model for rectangular nozzle openings in micro dimensions proposes an influence of the nozzle shape on the generated microbubble
7.1 Major outcomes

size. This theory was approved by numerical simulations and experiments. Rectangular nozzles generate up to 8% smaller monodisperse microbubbles than quadratic nozzles with the same cross sectional area, depending on the investigated flow rates. Furthermore, the orientation of the rectangular nozzle with respect to the liquid flow direction has an impact on the bubble size. Hence, the nozzle with the narrow side in the liquid flow direction exhibits up to 3% smaller monodisperse microbubbles than an equivalent nozzle with the wide side in flow direction. This performance was observed for inverted and truncated pyramid-shaped nozzle channels realized with KOH and straight rectangular nozzle channels fabricated with DRIE. The results were comparable but the KOH nozzles are superior due to their sloped side walls. These walls facilitate a workable coating of the nozzle with a 25 μm thick chemically inert nickel layer which is preferable for further use in the direct fluorination microreactor.

A novel and simple microfabrication method was developed for electrochemical metal deposition inside a microfluidic structure. This patent-pending process enables postforming of silicon-based microfluidic systems with a homogeneous, gas tight, and fluorine-inert nickel layer. Moreover, this nickel layer sufficiently bonds different substrate layers of the microfluidic system and therefore simplifies the microreactor fabrication process. Subsequently, selective KOH etching of the silicon substrate allows a release of the metal micropipes. That facilitates a characterization of the mechanical and chemical stability of the micropipes for a further use in the microreactor: The approximately 25 μm thick nickel layers homogeneously postformed the microchannels and were gas tight up to 6 bar.

A minireactor system for the direct fluorination of organic solvents was established. This system was used for pilot tests of the multiphase bubble flow, an active heat sink design, the nickel passivation and the bonding concept during the direct fluorination of ethylene carbonate (EC). The minireactor ran over 100 h process time with fluorine concentrations up to 88%. No leakage or corrosion of the nickel cover was detected over this period. Temperature measurements showed a sufficient cooling of the highly exothermic reaction which occurs within a short time of 36 ms and, therewith, in a restricted hot spot area of the reactor. The reaction conditions in the continuous flow minireactor were stable and resulted in high reaction yields of 79% with a fluorine conversion of 95%. This is clearly superior compared to the state of the art in EC direct fluorination with low fluorine concentrations of 30% that react to maximum yields and conversions of 63% and 59%, respectively.

Numerical simulations for the reaction microchannel design demonstrated the benefits of an optimized zigzag design with rounded corners and geometric focusing for the very fast and exothermic multiphase reaction. This meander design indicates a relatively high mixing quality (0.39) and Nusselt number (13.6) with acceptable pressure loss (796 Pa) for toluene at $Re = 150$ which is essential for the microreactor. A micro heat sink was developed that provides an optimal heat dissipation (91%) emerging from the direct fluorination in the designed reaction microchannel.
7 Conclusion and outlook

The microfluidic units of bubble generation, reaction channel, active heat sink were integrated into a complete microreactor system and fabricated using the in-channel electroless nickel plating. For worst case scenario calculations, this microreactor system showed a sufficient heat dissipation with an acceptable maximum heat increase of 16 K at the worst hot spot. Therewith, all requirements for successful direct fluorination in silicon based microreactors are solved. This enable a realization of direct fluorination in the proceeding research work in this topic.

The innovative fabrication method of in-channel electroless plating opens completely new possibilities for MEMS and microfluidic technologies. Two promising applications for the use in a direct fluorination microreactor were analyzed in detail to confirm their advantages over comparable devices. This fabrication method facilitates 3D designed micropipes. These simple 3D micropipes with only three bends were compared with 2D equivalents for their mixing quality. The 3D structures showed a distinctive benefit of 150% to 170% better mixing quality at low Reynolds numbers \( Re < 200 \). Produced metal micropipes were partly released and thermal measurements showed their benefits compared to embedded microchannels. Three times higher heat flux densities and decreased response times allow an accurate control of the temperature only with a variance of the surrounding cooling flow rate. These two applications are an important advantage for direct fluorinations and other highly exothermic chemical reactions in microreactors.

7.2 Outlook

The presented achievements for the design and fabrication of a direct fluorination microreactor and the pilot tests in a minireactor system pave the way for further developments. In particular, this is a direct fluorination reaction in an advanced microreactor and, generally, these are numerous microfluidic and MEMS applications.

The next step of the project “Direct fluorination in microreactors” has to be the integration of the microreactor into the chemical process setup that was already used for the minireactor pilot tests in the laboratory of the project partner. The main focus to accomplish this task is a gas-tight sealing of the platform for the microreactor which is needed for the fluid connections. It will allow to check the performance of the integrated microreactor with reference to heat dissipation, corrosion, influence of the interfacial area, and fouling tests in the reaction microchannel during direct fluorination of e.g. ethylene carbonate.

This reactor is only a first iteration step towards a complete microreactor system that utilize the whole benefits of miniaturization and sensor integration. These benefits include the aspect of increased reaction performance due to optimized microfluidic components as well as the integration of sensors to monitor the critical reaction parameters that allow an active control of the reaction.

The already tested 3D mixing microchannels and the freestanding micropipes would be the first and most promising microfluidic applications for the direct fluorination
microreactor. The 3D channels would supply an enhanced mixing and the cooling performance of the freestanding micropipes would facilitate higher fluorine concentrations i.e. more reaction heat is allowed to be generated during the reaction. Moreover, these applications may have a future impact on other microfluidic/microreactor systems.

Furthermore, the new fabrication technology enables the direct integration of sensor elements at the metal micropipe walls. Temperature measurements would be a promising application for the direct fluorination microreactor. This sensor can be realized using integrated micro thermocouples fabricated with electrochemical deposition. The concept is schematically shown in Figure 7-1a where the nickel microchannel is the first part of the thermocouple and the copper electrode the second part. The microchannel is partly released from the silicon substrate and the copper electrode is electroplated on the nickel channel wall forming the thermocouple. Another sensor application for the microreactor is pressure sensing inside the channel. The elastic characteristics of the nickel channel wall can be used for a membrane deflecting under a differential pressure. Figure 7-1b schematically shows the concept of the pressure sensor. A laser beam is focused on the reflecting metal membrane and the deformation is detected with a photodiode or a charge-coupled device (CCD).

![Figure 7-1: Schematic of a reaction microchannel wall with an integrated (a) thermocouple and (b) pressure sensor.](image)

With an optically transparent access it would be possible to perform *in-situ* monitoring of the reaction with Raman or X-ray spectroscopy. Sapphire is fluorine-resistant, transparent and enables a mechanical stable bonding to silicon and metals. A sapphire die can be integrated as part of the reaction channel wall with the in-channel electroless plating process, see Figure 7-2a. Within this thesis, this integration method was already shown with pyrex glass in first experiments. Moreover, with this optical access, it is possible to integrate an optical sensor to track the injected microbubbles, see Figure 7-2b. The sensor contains a laserdiode and a photodiode setup that was already used for the microbubble detection. Emitted light of the laserdiode is reflected by the nickel channel wall and the photodiode detects the light depending on the passing bubbles. For further developments
this setup can also be used for an integrated optical spectroscopy of the reaction product.

These presented sensor concepts will enable an in-situ and precise evaluation of the reaction heat, reaction rate, and the diffusion progress of the fluorine microbubbles. Thus, it would be possible to design cascading micronozzles for bubble injection and to intensify the reaction yield of fluorinated organic compounds.

Beyond the application in the microreactor for direct fluorination the in-channel electroless plating provides numerous possible applications for further research. The fabrication method can be used to seal and bond microchannels into stacks of punched metal-sheets forming a microfluidic system. This construction is advantageous for high pressure applications as, for example, petrochemical reactions. Released metal microchannels facilitate an active deflection, actuated electromagnetically or by piezo actuators. Therewith, the microchannels can be used for active mixing or for mass flow measurements using the coriolis effect. Additionally, the active actuation can also be used with metal membranes for valves or micropumps. Beyond the applications for microfluidic structures it is possible to fabricate numerous MEMS structures. These are for example micromirrors, 3D microcoils, cantilevers in different profiles or springs.

Briefly summarized, the results of this thesis deliver all relevant technical features for integrated direct fluorination microreactors. Particularly, the novel fabrication method of the in-channel electroless plating paves the way for further developments and applications in microreaction engineering, microfluidics and MEMS.

Figure 7-2: Schematic of a microreactor with optical access via a fluorine resistant sapphire die. That die is integrated with the electroless plating process into the microchannel wall. (a) optical observation with Raman or X-ray spectroscopy. (b) Integrated optical setup for bubble detection or spectroscopy.
7.2 Outlook
Appendix

Fluorescence intensity curve

The measured fluorescence intensity ($E$) relative to the maximum possible intensity ($E_{\text{max}}$) of Eq (6.7) in subchapter 6.2 depends on the fluorescein (Fl) concentration. Furthermore, it depends on the pH value of the mixing solution. Therefore, the relative intensity ($E/E_{\text{max}}$) depends on the volume fraction $\phi_{\text{base}}$ [Eq (6.6), subchapter 6.2] and the pH value that can be calculated with

$$
\frac{E}{E_{\text{max}}} = (1 - \phi_{\text{base}}) \cdot \begin{cases} 
0 & : \text{pH} < 4 \\
1/3.4 \cdot (\text{pH} - 4) & : 4 \leq \text{pH} \leq 7.4 \\
1 & : \text{pH} > 7.4
\end{cases} \quad (A.1)
$$

where pH = 4 indicates the minimum and pH = 7.4 the maximum pH value that is possible with the used acid solution (pH = 10.5) and base solution (pH = 4). The pH value of this equation can be solved with a charge balance equation

$$
[H^+] + [(\text{Na}^+)_{\text{NaOH}}] + [(\text{Na}^+)_{\text{Na}_2\text{Fl}}] + [\text{H}_3\text{Fl}^+] = [\text{Cl}^-] + 2[\text{Fl}^2^-] + [\text{HFI}^-] + [\text{OH}^-] \quad (A.2)
$$

of the used fluorescence system that is combined with the mass balance equations. The concentrations ($C$) of all involved species are lower or equal to the saturation concentration. Therefore, the mass balance equations for sodium and chloride are given by:

$$
[(\text{Na}^+)_{\text{NaOH}}] = \phi_{\text{base}} \cdot C_{\text{NaOH}}, \quad (A.3)
$$

$$
[(\text{Na}^+)_{\text{Na}_2\text{Fl}}] = 2 \cdot \phi_{\text{acid}} \cdot C_{\text{Na}_2\text{Fl}}, \quad (A.4)
$$

$$
[\text{Cl}^-] = \phi_{\text{acid}} \cdot C_{\text{HCl}}. \quad (A.5)
$$

The sum of the concentrations of the three prototrophic forms of fluorescein must be equal to the total amount of added fluorescein-sodium:

$$
[\text{Fl}^2^-] + [\text{HFI}^-] + [\text{H}_2\text{Fl}] + [\text{H}_3\text{Fl}^+] = \phi_{\text{acid}} \cdot C_{\text{Na}_2\text{Fl}}. \quad (A.6)
$$
The concentration fractions of the charged fluorescein forms allows to express their concentrations in the charge balance equation by means of the dissociations constants, the fluorescein-sodium concentration and the base volume fraction. The concentration fractions are:

\[
m_{\text{Fl}^2-} = \frac{[\text{Fl}^2-]}{\varphi_{\text{acid}} \cdot C_{\text{Na}_2\text{Fl}}} \]

\[
m_{\text{Fl}^2-} = \frac{K_{\text{HFl}} \cdot K_{\text{H}_2\text{Fl}} \cdot K_{\text{H}_3\text{Fl}}}{[H^+]^3 + [H^+]^2 K_{\text{H}_3\text{Fl}} + [H^+] K_{\text{H}_2\text{Fl}} \cdot K_{\text{H}_3\text{Fl}} + K_{\text{HFI}} \cdot K_{\text{H}_2\text{Fl}} \cdot K_{\text{H}_3\text{Fl}}} \quad , \quad (A.7)
\]

\[
m_{\text{HFI}^-} = \frac{[\text{HFI}^-]}{\varphi_{\text{acid}} \cdot C_{\text{Na}_2\text{Fl}}} \]

\[
m_{\text{HFI}^-} = \frac{[H^+] K_{\text{H}_2\text{Fl}} \cdot K_{\text{H}_3\text{Fl}}}{[H^+]^3 + [H^+]^2 K_{\text{H}_3\text{Fl}} + [H^+] K_{\text{H}_2\text{Fl}} \cdot K_{\text{H}_3\text{Fl}} + K_{\text{HFI}} \cdot K_{\text{H}_2\text{Fl}} \cdot K_{\text{H}_3\text{Fl}}} \quad , \quad (A.8)
\]

\[
m_{\text{H}_2\text{Fl}^+} = \frac{[\text{H}_2\text{Fl}^+]}{\varphi_{\text{acid}} \cdot C_{\text{Na}_2\text{Fl}}} \]

\[
m_{\text{H}_2\text{Fl}^+} = \frac{[H^+]^3}{[H^+]^3 + [H^+]^2 K_{\text{H}_3\text{Fl}} + [H^+] K_{\text{H}_2\text{Fl}} \cdot K_{\text{H}_3\text{Fl}} + K_{\text{HFI}} \cdot K_{\text{H}_2\text{Fl}} \cdot K_{\text{H}_3\text{Fl}}} \quad . \quad (A.9)
\]

The hydroxide ion concentration can be expressed by the autoprotolysis constant \(K_w = 10^{-14}\). Thus, the hydroxide ion concentration is given by:

\[
[\text{OH}^-] = \frac{10^{-14}}{[H^+]}. \quad (A.10)
\]

According to the base volume fraction of Eq (6.7) in subchapter 6.2 the acid volume fraction of the base \((V_{\text{base}})\) and the acid \((V_{\text{acid}})\) is

\[
\varphi_{\text{acid}} = \frac{V_{\text{acid}}}{V_{\text{base}} + V_{\text{acid}}} = 1 - \varphi_{\text{base}} \quad , \quad (A.11)
\]

and can also be expressed by the base volume fraction.
The equations Eq (A.3) to Eq (A.10) are inserted into the charge balance Eq (A.2):

\[
[H^+] + \varphi_{\text{base}} \cdot C_{\text{NaOH}} + 2 \cdot C_{\text{Na}_2\text{Fl}} \cdot (1 - \varphi_{\text{base}}) \\
+ m_{\text{H}_2\text{Fl}} \cdot C_{\text{Na}_2\text{Fl}} \cdot (1 - \varphi_{\text{base}}) = C_{\text{HCl}} \cdot (1 - \varphi_{\text{base}}) \\
+ 2 \cdot m_{\text{Fl}^2} \cdot C_{\text{Na}_2\text{Fl}} \cdot (1 - \varphi_{\text{base}}) \\
+ m_{\text{HF}} \cdot C_{\text{Na}_2\text{Fl}} \cdot (1 - \varphi_{\text{base}}) + \frac{10^{-14}}{[H^+]} 
\]  

(A.12)

This equation involves the hydronium-ion concentration to the power of 5. This, has to be calculated with the help of Mathematica 7 (Wolfram Research, USA). With the solution of Eq (A.12) the pH value can be solved for the used fluorescein model. This pH value is inserted in Eq (A.1) to solve the theoretical relative fluorescence intensity \( E/E_{\text{max}} \) for the graph of Figure 6-6 in subchapter 6.2.
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