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Abstract

The topic of this project is the design and fabrication of chemical microreactors with short response time and high sensitivity to low catalyst areas. The microreactors are intended as analytical tools in experiments concerning heterogeneous catalysis, photocatalysis, and electrocatalysis. The reactors consist of a microchannel system etched in an oxidized silicon chip and sealed with a glass lid using anodic bonding. The chip design relies on a gas flow through the channel system and is designed for reactions at pressures at the order of 1 bar. A high sensitivity is obtained by directing the entire gas flow through the reaction zone to a mass spectrometer, thus ensuring that nearly all reaction products are present in the analyzed gas flow.

An experimental study has been carried out of the conditions for cavity collapse during anodic bonding of wide, shallow grooves etched in silicon. The aim of this study has been to determine appropriate dimensions for the reaction chamber in the microsystem. It has been found that 200 \( \mu \)m diameter circular silicon pillars distributed in the chamber are effective in preventing cavity collapse in such grooves. In particular, the pillars allow anodic bonding without collapse of 3 \( \mu \)m deep, 1 cm diameter circular reaction chambers.

During the project, a microreactor has been developed for photocatalysis and heterogeneous catalysis in gas phase reactions. To demonstrate the operation of the microreactor, CO oxidation on low-area platinum thin film circles has been employed as a test reaction. Using temperature ramping, it has been found that platinum catalysts with areas as small as 15 \( \mu \)m\(^2\) are conveniently characterized with the device.

A setup for locally cooled anodic bonding of microreactors is presented. The aim with this setup is to avoid catalyst deactivation in the reactor during bonding. A finite element analysis has been carried out to investigate the temperature distribution during bonding in a microreactor. The analysis suggests that the setup can effectively keep the reaction chamber temperature below 50 °C while the rest of the chip bonds. This is in good agreement with direct temperature measurements.

A two-phase mesh microreactor has been developed, in which a gas and a liquid phase can be brought into contact. The reactor is intended for characterization of photoelectrode materials in photoelectrolysis, and the gas-liquid-interface is stabilized by a highly perforated, hydrophobic silicon membrane. The device allows measurements of electrode current simultaneously with direct product detection. The operation of the device has been demonstrated employing electrolysis of water as a test reaction.

Et eksperimentelt studie er blevet udført for at studere betingelserne for kollaps af kaviteter under anodisk sammenføjning med brede, lave forsænkninger øset i silicium. Formålet med dette studie har været at bestemme passende dimensioner for reaktionskammeret i mikrosystemet. Det har vist sig, at tilstedeværelse i kammeret af cirkulære siliciumsøjler med en diameter på 200 μm effektivt forhindrer kollaps af kaviteter i sådanne forsænkninger. Specielt tillader søjlers tilstedeværelse anodisk sammenføjning uden kollaps af 3 μm dybe, cirkulære reaktionskamre med en diameter på 1 cm.

I løbet af projektet er en mikroreaktor blevet udviklet til fotokatalyse og heterogen katalyse i gasfase-reaktioner. CO oxidation på platin-tyndfilms-cirkler er blevet anvendt som en testreaktion for at demonstrere mikroreaktorens virkemåde. Ved brug af temperaturrampning er det blevet påvist, at platinkatalysatorer med arealer på kun 15 μm² praktisk kan karakteriseres med chippen.

En opsætning til anodisk sammenføjning med lokal køling præsenteres. Formålet med opsætningen er at undgå deaktivering af katalysator i reaktoren under sammenføjningen. En finite element-analyse er blevet udført for at undersøge temperaturfordelingen i mikroreaktoren under sammenføjning. Analysen indikerer, at opsætningen giver anledning til en temperatur i reaktionskammeret på under 50 °C mens resten af chippen sammenføjes. Dette resultat er i god overensstemmelse med direkte temperaturmålinger.

Preface

This PhD dissertation describes a PhD project carried out at the Department of Micro- and Nanotechnology (DTU Nanotech) at the Technical University of Denmark (DTU). The dissertation is submitted in partial fulfillment of the requirements for obtaining the PhD degree from this university. The research reported has been conducted in the period from February 2007 to April 2010. The project has been supervised by Associate Professor Ole Hansen and financed by a grant from DTU. The project has been carried out as part of the microreactor activities in the interdisciplinary research group Center for Individual Nanoparticle Functionality (CINF) which consists of researchers from DTU Nanotech and the Department of Physics at DTU. Among many other activities CINF conducts research in microreactor design and fabrication and applies microreactors as analytical tools in experiments concerning catalysis and surface science.

This project has been part of a combined effort at CINF to develop microreactor platforms for catalyst characterization. Thus, during the project I have cooperated closely with other researchers at CINF, and in some cases the role of my work can best be understood in the context of contributions from my colleagues. Hence, to give a complete and satisfactory account of my project, in some parts of this dissertation I have included experimental work which has been carried out by my associates at CINF. My own responsibilities in the combined endeavors have among other things comprised extensive design and cleanroom fabrication of microsystems, finite element simulations and other types of modeling, in addition to analysis of experimental data.

A summary of experimental work of my colleagues presented in this thesis is given in the following. The experimental setup described in section 2.5 has in large parts been designed and built by my fellow PhD students Peter Vesborg and Jakob Olsen, who have both made vital contributions to advance the microreactor activities at CINF. The pump down experiment described in section 3.3 was likewise carried out by Peter and Jakob, although the evaluation of experimental data presented in that section is my own contribution. The catalytic activity measurements presented in section 3.4.2 were carried out by Jakob; however, I have been deeply involved in the analysis of experimental data. The photocatalytic activity measurements described in section 3.5 were carried out by Peter. Jakob and Peter designed and set up the arrangement for locally cooled anodic bonding described in section 4.1, and they also performed the temperature measurements presented in section 4.2.2. The finite element simulation described in chapter 4 is my own contribution. Finally, the experiments with electrolysis of water presented in section 5.3 were done by Jakob and Peter. The remainder of the work presented in this dissertation (the parts not explicitly mentioned above), I have been deeply involved in personally.
Many people have helped and supported me during the project, and I will take the opportunity to thank some of them here. First of all I would like to thank my advisor Ole Hansen for competent guidance and invaluable assistance throughout the project. I would also like to thank Professor Ib Chorkendorff from CINF for many helpful discussions in the course of the project and for good advice regarding authoring of journal articles.

I thank former Post Doc Søren Jensen for introducing me to cleanroom work and for passing on his extensive knowledge about microreactors when I first started on the project. Throughout the project I have benefitted from processing assistance from Danchip laboratory technician Conny Hougaard, who has also offered invaluable assistance with fabricating microreactors for me and my colleagues at CINF, often at a short notice. I would also like to thank the Danchip staff in general, whose friendliness and readiness to help have been very much appreciated.

I thank my fellow PhD students Peter Vesborg and Jakob Olsen for good cooperation during the past three years. Peter and Jakob have come up with many creative and fruitful ideas which have often taken the microreactor activities at CINF in exciting, unexpected directions. I have enjoyed working with former Post Doc Adam Monkowski, who was always willing to share his vast knowledge of microfabrication and to provide practical help in the cleanroom. Adam is also credited for promptly coming up with the idea for the mesh microreactor, at a time when our efforts to convert the existing reactor to include a liquid phase seemed to have been faced with insurmountable difficulties. Thanks are also due to Post Doc Thomas Pedersen with whom I fabricated the first batch of mesh microreactors. His expertise and tenacity were very valuable at this critical stage of the project.

I would also like to thank everyone at CINF and DTU Nanotech, whose help has not necessarily been of a technical nature but who has contributed to the enjoyable working environment. I will miss having lunch with Anders Greve, Jesper Olsen, Asger Vig, and Claus Jeppesen in our joint lunch club. During my project I have had the pleasure of sharing my office with a diverse and international group of people. Thus, I would like to thank Yanxin Zhuang, Peder Skafte-Pedersen, Joanna Lopacinska, Eric Jensen, Thomas Buss, and Giulio Fragiacomo for a good atmosphere in the office and for helping with all the little things.

Outside the world of DTU, I would like to thank all the good people I know from my dormitory Studentergaarden, which has been my home throughout my PhD studies and a safe base to return to after working long hours in the cleanroom. Finally, I warmly thank my family and friends for all their support and patience. Their advise and encouragement have been very important to me during the entire project.

Kongens Lyngby, April 30th, 2010

Toke Riishøj Henriksen
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Chapter 1

Introduction

The topic of this project is the design and fabrication of chemical microreactors for measurements of catalytic activity and surface kinetics. The devices are intended as analytical tools for development of new catalysts as well as for fundamental studies of chemical reactions. The primary aim has been to produce novel, continuous-flow microreactors with high sensitivity to low amounts of reaction products. Batch microfabrication techniques are used to produce the reactors, which are made of silicon and Pyrex glass. The project has focused on the development of two different types of reactors, suitable for gas phase and liquid phase reactions, respectively. The aim has been to produce reactors well-suited for studies of heterogeneous catalysis as well as for electrolysis and photochemistry.

In this chapter the PhD project is introduced, and the scope and objectives of the project are presented. A brief review of heterogeneous catalysis, electrolysis, photochemistry, and chemical microreactors is given. These concepts are all at the heart of the project. The introduction is concluded with an outline of the dissertation.

1.1 Heterogeneous catalysis

A catalyst is a substance that increases the reaction rate of a chemical reaction without itself undergoing chemical change in the process. Catalysis is the action of a catalyst. Catalysis is of fundamental importance in modern society, among other things because approximately 85-90% of the products in the chemical industry are synthesized in catalytic processes [1].

Catalytic reactions can be characterized by the nature of the catalysts, reactants, and products involved. Of special interest in this project is heterogeneous catalysis where the catalyst is a solid, and the reactants are either in gas or liquid phase. The reaction takes place on the surface of the catalyst. Heterogeneous catalysis is widely used in the chemical industry, and essential products such as ammonia (used to produce fertilizers), methanol (a raw material in the production of plastics and many other materials), and ethylene glycol (employed as antifreeze material in automobiles) are all produced using heterogeneous catalytic processes [1]. Heterogeneous catalysis is also used in the processing of crude oil for production of e.g. gasoline. In addition, heterogeneous catalysis is imperative in
environmentally friendly technologies such as in the cleaning of flue gases from power plants and the cleaning of automotive exhaust.

Heterogeneous catalysis is likely to play an important role in solutions to the potential energy crisis which might arise in the future, when fossil fuel reserves start to dwindle. Modern society relies heavily on fossil fuels for the production of energy. The most important reserves of fossil fuels available to humankind are oil, natural gas, and coal. These are all nonrenewable resources, and the known reserves of oil and gas will most likely be depleted within the next 60 years. Even though new oil and gas fields are still being discovered, these two fossil fuels will eventually be depleted all together. The world’s coal reserves are expected to last significantly longer than the oil and gas reserves [1]. Consequently, when oil and gas are no longer available, hydrocarbons for e.g. liquid fuels might have to be produced from coal through the processes known collectively as Fischer-Tropsch synthesis. Heterogeneous catalysis plays an essential role in this technology. It is clear that heterogeneous catalysis is of paramount importance for modern society today and will continue to be so in the future.

Since the reaction occurs on the surface, and catalyst materials are often expensive, it is favorable with a high surface area to volume ratio of the active phase. Thus, the majority of the catalysts used in industrial heterogeneous catalysis are nanoparticles (often transition metals) dispersed on a high-surface-area, porous support material. These nanoparticles typically have dimensions of 1 to 20 nm [2]. As an example, in ammonia synthesis, molecular hydrogen and nitrogen react to form ammonia

\[ \text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g). \] (1.1)

The catalyst most often used in industry for this reaction consists of iron dispersed on the oxides of aluminum, calcium, and potassium [3].

The morphology of a nanoparticle catalyst can have a dramatic effect on the catalytic activity. For instance, gold is completely inactive for oxidation of carbon monoxide at room temperature, unless the gold is in the form of particles smaller than \( \sim 8 \) nm in diameter [4, 5]. As seen in Fig. 1.1 gold nanoparticles exhibit a marked increase in catalytic activity for this reaction when the diameter is reduced below 3.5 nm. A further reduction in the particle diameter below \( \sim 3 \) nm leads to a decrease in the catalytic activity [6]. It appears that in this case the exact particle size greatly affects the catalytic properties. The activity at room temperature makes gold nanoparticles a potential candidate for carbon monoxide oxidation catalysts in automobiles. Today, most carbon monoxide pollution from automobiles is emitted in the first five minutes after startup. This is because platinum- or palladium-based catalysts currently used in automobile exhaust cleanup are inactive below 200°C [4]. Gold nanoparticles with a size finely tuned for low temperature carbon monoxide oxidation is a potential solution to this environmental problem.

The correlation between the morphology and catalytic activity of nanoparticles is a topic of considerable scientific interest, both from a fundamental and an application-oriented point of view [7–9]. One approach to such studies is to produce ensembles of nearly identical nanoparticles and measure the variation of catalytic activity with particle size. Such model catalysts can for instance be obtained as mass selected nanoparticles from a magnetron sputtering cluster source. Alternatively, samples of nearly identical
1.2 Electrolysis

Electrolysis is an electrochemical process where electrical energy is supplied to a system to effect a non-spontaneous reaction. In electrolysis a pair of electrodes are immersed in an electrolyte which contains the reactants. When a sufficiently large voltage difference is applied between the electrodes, the reaction proceeds, and the products are formed at the electrodes. A well-known example is the electrolysis of water, where water is split into hydrogen and oxygen

\[ 2H_2O(l) \rightleftharpoons 2H_2(g) + O_2(g). \]  \hspace{1cm} (1.2)
Hydrogen and oxygen are formed at the negative and positive electrode, respectively. For many applications, the reaction rate in electrolysis must be enhanced by the presence of electrocatalysts, which can be present on the electrode surfaces or, alternatively, can be the electrodes themselves.

Electrolysis has many important applications today, among other things for hydrogen production. In addition, it has potential applications relating to the search for sustainable energy systems. The development of renewable and CO₂ neutral energy systems is one of the most important scientific challenges of our age. Such energy solutions must eventually rely on the energy associated with the electromagnetic radiation emitted from the sun. This radiation is the ultimate source of wind and wave energy, and the solar radiation can also be utilized directly. Today, one of the main obstacles against the efficient utilization of wind, wave, and solar energy is the large temporal variations characteristic for these sources. Wind turbines only produce electricity when it is windy, and solar cells are only productive when the sun shines. Thus, there is a call for convenient methods for storing the energy obtained from these sources. An expedient solution would be to store the electricity produced by e.g. wind turbines and photovoltaic cells as chemical energy by effecting non-spontaneous reactions through the use of electrolysis. The reaction products would act as energy carriers. Potentially attractive processes include the conversion of carbon dioxide into liquid fuels such as methanol, or the conversion of nitrogen from the air into ammonia. One of the main challenges with such electrochemical processes is the development of effective and inexpensive electrocatalysts.

1.3 Photochemistry

Photochemistry is the study of chemical reactions which are initiated by electromagnetic radiation, usually visible or ultraviolet (UV) light. Photochemical reactions can be either spontaneous or non-spontaneous. For spontaneous reactions the photon energy is spend on overcoming activation energies, and in non-spontaneous reactions the photon energy is stored as chemical energy in the products. Many photochemical reactions proceed under influence of a photocatalyst. A photocatalyst is a substance that is able to produce, by absorption of photons, photochemical reactions without itself being consumed in the process. An important type of photocatalysts is semiconductors, which upon absorption of photons create electron-hole pairs which subsequently reduce and oxidize the reactant (see Fig. 1.2). Photoelectrolysis is a chemical process where both electrical energy and electromagnetic radiation are supplied to a system to effect a non-spontaneous reaction. This is similar to electrolysis, but the surface of one of the electrodes contains a semiconductor photocatalyst (see Fig. 1.3). Electron-hole pairs are generated upon absorption of light. Band bending at the semiconductor-electrolyte interface causes minority carriers in the semiconductor to move towards this interface, while majority carriers move towards the semiconductor bulk. Redox couples in the electrolyte capture the photogenerated carriers and the reactions occur. The external bias and the counter electrode are required for matching the electron and hole energies with the redox potentials associated with the reaction.
1.3 Photochemistry

Figure 1.2: Scheme for water splitting catalyzed by a semiconductor photocatalyst. The reaction is effected by UV radiation of a colloidal suspension of a semiconductor in water. Metallic catalysts have been co-deposited on the exterior surface of the semiconductor. Strontium titanate, by virtue of its electron structure, is an example of a semiconductor capable of effecting photocatalytic dissociation of water under UV irradiation.

Figure 1.3: Illustration of photoelectrolytic water splitting using n-type titanium dioxide as a photoanode and platinum as a counterelectrode. A power supply must be included in the external circuit to match the electron and hole energies with the redox potentials associated with the reaction. Figure acquired from [3].
Photocatalysis can among other things be used to degrade environmentally harmful compounds with oxygen as oxidizing agent and titania as catalyst. In addition, photocatalysis could potentially be a convenient way of directly storing the energy from the solar radiation as chemical energy. An especially attractive reaction which has received much scientific interest is the photoelectrolytic splitting of water. This would be a very useful way of producing hydrogen from water (an abundant resource) with no carbon dioxide emissions. Other attractive photoelectrolytic reactions include the conversion of carbon dioxide and hydrogen into methanol and the conversion of nitrogen and hydrogen into ammonia. Thus, there are prospects of solar energy being used photochemically to produce fuels and chemical feedstocks, all derived from water [3] and with no net carbon dioxide emissions (see Fig. 1.4).

1.4 Chemical microreactors

The main topic in this thesis is chemical microreactors for analyzing chemical reactions and surface physics. The term 'microreactor' is sometimes used with different meanings in different contexts. The definition used in this thesis is that a microreactor is a chemical reactor with dimensions in the micrometer range [15]. Traditionally, macroscale chemical reactors such as the idealized plug flow reactor have been used in chemistry for applications such as catalyst characterization and optimization of reaction conditions [1]. As a supplement to these traditional reactors, microreactors have in recent years shown promise as versatile analytical tools for such studies. Thus, microreactors have been shown to offer a number of advantages compared to conventional macroscale reactors [15–22]. Due to the high surface-to-volume ratio, heat transfer to and from the reaction zone is greatly enhanced. This reduces temperature differences in the reactor and makes accurate control of temperature possible, even for strongly exothermic reactions. The low heat capacity of the device facilitates easy and quick variations of the reaction zone temperature. Furthermore, the small dimensions of the reactor improve mass transfer and reduce concentration gra-
1.4 Chemical microreactors

Figure 1.5: Sketch of a “T”-type microreactor. A “T”-formed structure has been etched into the substrate. Reagents are introduced through the top-left and top-right point of the “T” and proceed to the trunk of the “T” where they react. Products leave the reactor through the outlet at the bottom point of the “T”.

dients. Small thermal and concentration gradients are favorable when determining kinetic data. Reaction parameters such as pressure, residence time, and flow rate are more easily controlled in reactions that take place in small volumes. In addition to these advantages, the small scale of the reactor improves safety of use for explosive mixtures and greatly reduces reactant consumption. Finally, it is possible to integrate heaters and sensors directly into microreactors using microfabrication technology.

Fundamentally, a continuous-flow microreactor consists of a system of microchannels in which the reactants will flow and react. One of the simplest forms of a microreactor is the “T”-reactor, which is sketched in Fig. 1.5. It consists of a “T”-shaped system of microchannels etched into a plate (typical materials include stainless steel and silicon). The microchannels typically have dimensions in the range of $1 \text{ – } 500 \, \mu m$ and are sealed from above by bonding a plate on top of the original one. Inlets are produced and are aligned with the top-left and top-right point of the “T”. Likewise, an outlet is produced, aligned with the bottom point of the “T”. Two different reactant mixtures can now be introduced into the reactor through the two inlets and proceed to the reaction chamber in the trunk of the “T”, where they mix and react. Products from the reaction can be obtained through the outlet. The microreactors presented in this thesis are a variation of this “T”-reactor concept. The flow through the microchannels is mostly laminar, resulting in predictable and well-controlled flow patterns. Due to the small dimensions, the residence time of the reactant fluid in the catalyst bed is typically low. Consequently, high space velocities and short response times can be obtained.

Of special interest in this thesis is the high sensitivity of microreactors in gas phase reactions, even at pressures at the order of one atmosphere. In combination with an appropriate instrument for gas composition analysis, it is possible to design microreactors which facilitate detection of very small amounts of gas species at high pressures. The
low gas flow rate through the microchannel system drastically limits dilution of reaction products. Thus, the minimum absolute reaction rate required to raise the product concentration above the detection level is reduced correspondingly. High sensitivity product detection under atmospheric pressure is especially useful for measuring the catalytic activity of model catalysts with low surface areas.

The high sensitivity of microreactors also opens up new possibilities in other surface chemistry studies, such as experiments with temperature programmed desorption (TPD). Conventional TPD experiments can be performed on single crystal surfaces under ultra high vacuum (UHV) conditions where the desorbing atoms or molecules are directly detected with a mass spectrometer. Single crystal surfaces can be characterized in great detail, which is a significant advantage of this method. Alternatively, desorption into a carrier gas at high pressure is possible. In this case, the atoms and molecules desorb into the carrier gas, which is subsequently analyzed. Desorption into a carrier gas is generally well-suited for high surface-area materials such as industrial catalysts; however, single crystal surfaces are generally excluded from this method. A monolayer of molecules on a flat nonporous surface desorbing into a carrier gas will usually be well below the detection limit. Thus, there is a gap between the two techniques: The UHV-TPD can be performed on well-characterized single crystal surfaces, but only under vacuum conditions. This means that only desorption of molecules can be measured. TPD in a carrier gas can be performed under high pressure, which represents more realistic conditions and makes it possible to study both adsorption and desorption as well as equilibrium properties between adsorbed molecules and molecules in the gas. However, this method is only suitable for porous surfaces which are difficult to characterize in detail. Microreactors show promise as useful tools to perform TPD in a carrier gas even for single crystal surfaces, thus bridging the gap between the traditional methods. Hence, it has been shown that the high sensitivity of microreactors makes it possible to detect carbon monoxide desorbing from a 0.5 cm² area of platinum in an argon carrier gas at atmospheric pressure [23].

Microreactors can be produced using microfabrication batch techniques. These manufacturing processes employ photolithography and subsequent etching techniques to form patterns in a substrate, such as a silicon wafer. The etching methods can for instance be reactive ion etching (RIE) and deep RIE (DRIE), which are both plasma dry etching processes. DRIE is a technique with which deep and narrow structures with vertical side-walls can be etched in silicon [24]. Using such micromanufacturing batch techniques, large numbers of devices can be produced in a short time and at relatively low cost. Microfabrication techniques were originally developed in the microelectronics industry for producing silicon integrated circuits. In the last few decades the same processes have found increasing use in the fabrication of other types of Microsystems, where the small scales of the structures are an inherent advantage. Such Microsystems, also known as microelectromechanical systems (MEMS), can combine electrical, mechanical, optical, and fluidic components in a single device. The microreactors presented in this thesis are an example of such a microsystem. In particular, the microreactors developed in this project consist of a microchannel system etched in a silicon chip and sealed with a Pyrex lid using anodic bonding. The silicon chip is the actual microsystem, which is produced using microfabrication techniques. The catalyst is deposited in a reaction chamber on the silicon
chip prior to bonding. Subsequently, the silicon chip is sealed with the glass lid. Thus, the Pyrex lid is not part of the microsystem but should rather be considered part of the application.

As outlined in this introduction, microreactors offer several advantages compared to conventional macroscale reactors. In this thesis, the primary motivations for employing microreactors are the virtues of higher sensitivity and shorter response time relative to conventional reactors. The high sensitivity allows measurements on very small amounts of catalytic material. For many experiments, the short response time drastically reduces the time consumption compared to conventional macroscale reactors. Thus, one of the most important aims of this project has been to develop reactors well-suited for measuring the catalytic activity of size selected catalytic nanoparticles. The samples are produced with a magnetron sputtering cluster source, and the goal is to correlate the morphology and catalytic activity of the nanoparticles. Only small quantities of nanoparticles can be deposited per unit time, and in addition the number of nanoparticles is often kept low to suppress sintering effects. Thus, a highly sensitive microreactor could be very useful in such experiments. The reactors designed in this project are also intended for use in experiments concerning photocatalysis and photoelectrolysis. The motivation for employing microreactors to measure the activity of photocatalysts is related to the high sensitivity and short response time. Monochromatic light sources are often used to study the dependence of photocatalytic activity on wavelength (this dependence is known as the action spectrum). Monochromatic light sources tend to have a lower intensity than broad band sources, so a highly sensitive measurement technique is desirable in these experiments. In addition, the short response time can be a significant advantage in measurements of photocatalytic activity. This is because a high time resolution facilitates mechanistic information on adsorption, desorption, and mass transfer. Furthermore, a short response time allows fast, quantitative measurements of photocatalytic activity as a function of illumination intensity and wavelength.

1.5 Dissertation outline

This dissertation is divided into six chapters and one appendix. In the following an outline of the remainder of the thesis is given.

- **Chapter 2**: An overview of the generic microreactor design is given. This chapter describes features which are common to all microreactors fabricated in the project. The chapter contains a brief review of gas dynamics and mass transfer in a gas mixture and presents the basic concepts and reasoning behind the generic reactor design.

- **Chapter 3**: This chapter presents a microreactor for gas phase reactions intended for use in experiments with photocatalysis and heterogeneous catalysis. It is explained how this microreactor is based on the generic design, and a description of the design and fabrication is given. The results of catalyst experiments employing the microreactor are presented to demonstrate the operation of the device.
• **Chapter 4:** A method for carrying out anodic bonding with local cooling is presented. It is described how this procedure facilitates anodic bonding of the microreactors while maintaining a low temperature at the position of the catalyst. This is useful for preventing catalyst deactivation during the process. A finite element analysis of the temperature distribution in the reactor during bonding is presented and compared to direct temperature measurements.

• **Chapter 5:** This chapter presents a two-phase microreactor in which a gas and a liquid phase can be brought into contact. The reactor is intended for characterization of photoelectrode materials in photoelectrolysis. It is explained how this microreactor is based on the generic design, and a description of the design and fabrication is given. The results from tests of the reactor are evaluated.

• **Chapter 6:** A conclusion on the project as a whole is given and the most important results are stated. Also, an outlook on the perspectives of the project is given.

• **Appendix A:** This appendix contains a number of contributions to various scientific journals. These manuscripts describe some of the results of the project.
Chapter 2

Generic microreactor design

The microreactors presented in this dissertation all share the same fundamental design, which includes choice of materials, footprint, microchannel system topology, and gas composition analysis method. This basic concept has been selected for the purpose of obtaining high sensitivity and high space velocity in the reaction zone. In this chapter, the generic design is described and analyzed with reference to optimizing device performance.

First, the theory of gas flows in microchannels is reviewed. This topic plays a significant role in the thesis, since all the microreactors designed in this project rely on gas flow through ducts with cross sectional dimensions in the micrometer range. In addition, fundamental design issues are examined, such as the requirements to a microreactor for detecting gas species that are produced at low rates. This chapter also presents the basic topology of the microchannel system employed in this project. Finally, the experimental setup used for microreactor experiments is described.

2.1 Bulk gas motion

In this section, the fundamental theory of gas flows through microchannels is described. At first, the different gas flow regimes which can occur in microchannels are discussed. Subsequently, analytical expressions are presented for gas flows through microchannels with different cross sections and in different flow regimes.

2.1.1 Gas flow regimes

Gas flow through microchannels can be more complicated than for macroscopic channels, since the small cross sectional dimensions might be comparable to the mean free path of the gas, resulting in noncontinuum flow regimes. Gas flow in a tube of characteristic cross sectional width $d$ can be characterized by the Knudsen number $Kn$, which is defined as

$$Kn = \frac{\lambda}{d},$$

(2.1)

where $\lambda$ is the mean free path of molecules in the gas.

The mean free path is given by
2. Generic microreactor design

\[ \lambda = \frac{k_B T}{\sqrt{2\pi s^2 p}}, \quad (2.2) \]

where \( k_B \) is Boltzmann’s constant, \( T \) is the temperature, \( p \) is the pressure, and \( s \) is the molecular diameter.

The nature of the gas flow is determined by the value of the Knudsen number. In general, three different flow regimes can be distinguished, as outlined below.

- \( Kn < 0.01 \): Continuum flow. The flow is dominated by collisions between two gas molecules. This situation is similar to flow through macroscopic ducts.

- \( 0.01 < Kn < 1 \): Intermediate flow. Two different kinds of collisions both contribute significantly to the nature of the flow. The first kind is collisions in between two gas molecules. The second kind is collisions between a single gas molecule and the walls of the duct.

- \( Kn > 1 \): Molecular flow. The flow is dominated by collisions between a single gas molecule and the walls of the duct.

If the flow is in the continuum regime, it can be characterized by Reynold’s number \( Re \), which is defined as

\[ Re = \frac{u \rho D_h}{\eta}, \quad (2.3) \]

where \( u \), \( \rho \), and \( \eta \) are the velocity, mass density, and viscosity of the gas, respectively. \( D_h \) is the hydraulic diameter which is given by

\[ D_h = \frac{4A}{P}, \quad (2.4) \]

where \( A \) is the cross sectional area, and \( P \) is the perimeter of the cross section.

For flow through ducts, when \( Re > 2200 \), the flow is always turbulent, and when \( Re < 1200 \), the flow is always laminar. In the regime \( 1200 < Re < 2200 \) the flow is either laminar or turbulent, depending on the geometry of the inlet and outlet and on the nature of the piping irregularities [25].

2.1.2 Gas flow rate

The gas flow rate \( \dot{N} \) is defined as the net absolute number of gas molecules crossing a cross section of the channel per unit time. In the following, analytical expressions will be presented for the gas flow rate through channels of different cross sectional dimensions and for different flow regimes. Ideal gas behavior will be assumed. In the context of this section, the flow conductance is an important quantity, which relates the gas flow rate to the pressure difference \( \Delta p \) across the channel. In this thesis, the flow conductance \( C \) is defined as the ratio between the gas flow rate and the pressure difference, so \( C = \dot{N}/\Delta p \). The inverse of the flow conductance is known as the flow resistance.
2.1 Bulk gas motion

Figure 2.1: Coordinate system for gas flow in a channel, which is translationally invariant in the $x$ direction, and that has an arbitrarily shaped cross-section in the $yz$-plane. The pressure at the left end, $x = x_1$, is an amount $\Delta p$ higher than at the right end, $x = x_2$.

Figure 2.2: Coordinate systems for two specific channel cross sections used in description of gas flow in long, straight channels. (left) Circle with radius $a$. (right) Rectangle of height $h$ and width $w$. Both figures acquired from [26].

We will now consider continuum, laminar gas flows through cylindrical channels with circular and rectangular cross sections. Let the axis of the cylinder be parallel to the $x$-axis (see Fig. 2.1 and 2.2). Then the pressure inside the channel varies with $x$ but is independent of the spatial coordinates $y$ and $z$. In general, $dp/dx$ also varies with $x$. The average velocity $\mathbf{u}$ of the gas molecules is parallel to the $x$-axis everywhere and can thus be designated by its $x$-component $u_x$.

For continuum, laminar gas flow through a channel with circular cross section of radius $a$, the velocity field is given by [27]

$$u_x(x,y,z) = \frac{1}{4\eta} \frac{dp}{dx} (a^2 - y^2 - z^2). \quad (2.5)$$

The corresponding gas flow rate is given by [25]

$$\dot{N} = \frac{1}{k_B T} \frac{\pi a^4}{8\eta \ell} \hat{p} (p_1 - p_2), \quad (2.6)$$
Figure 2.3: (a) Contour lines for the velocity field \( u_x(y,z) \) for continuum, laminar fluid flow in a long, straight, rectangular channel. The contour lines are shown in steps of 10% of the maximal value \( u_x(0,h/2) \). (b) A plot of \( u_x(y,h/2) \) along the long centerline parallel to the \( y \)-axis. (c) A plot of \( u_x(0,z) \) along the short centerline parallel to the \( z \)-axis. Figure acquired from [26].

where \( \ell \) is the length of the channel, \( p_1 \) and \( p_2 \) are the pressures on the high and low pressure sides, respectively, and \( \bar{p} = (p_1 + p_2)/2 \).

For continuum, laminar gas flow through a channel with rectangular cross section, the velocity field is given by [26]

\[
 u_x(x,y,z) = \frac{4h^2}{\pi^3 \eta} \frac{dp}{dx} \sum_{n, \text{odd}} \frac{1}{n^3} \left[ 1 - \frac{\cosh(n\pi \frac{y}{h})}{\cosh(n\pi \frac{w}{\bar{h}})} \right] \sin \left( n\pi \frac{z}{h} \right),
\]

a series containing only positive, odd integers \( n (n = 1,3,5,\ldots) \). \( h \) is the height or width, whichever is smaller, and \( w \) is the height or width, whichever is larger. The velocity field given by Eq. (2.7) is plotted in Fig. 2.3.

The corresponding gas flow rate is given by [26, 27]

\[
 \dot{N} = \frac{1}{k_B T} \frac{wh^3}{12\eta \ell} \left[ 1 - \sum_{n, \text{odd}} \frac{192}{n^5} \frac{h}{\pi^5} \frac{\tanh(n\pi \frac{w}{2h})}{\tanh(n\pi \frac{w}{2\bar{h}})} \right] \bar{p}(p_1 - p_2).
\]

For \( w \gg h \) an approximate expression can be found by determining the limit \( h/w \to 0 \) in Eq. (2.8). One obtains [26, 27]

\[
 \dot{N} \approx \frac{1}{k_B T} \frac{wh^3}{12\eta \ell} \left( 1 - 0.630 \frac{h}{w} \right) \bar{p}(p_1 - p_2).
\]

Eq. (2.9) is a very good approximation in many cases. In the worst case where \( w = h \), the error is 13%, while for \( h = w/2 \), the error is only 0.2%. It is clear from Eq. (2.6) and (2.8), that in both cases the flow conductance is proportional to \( \bar{p} \), the mean of the pressures on each end of the channel.

We now consider noncontinuum flow regimes. For intermediate flow through a channel with circular cross section, the gas flow rate is given by [28]
\[ 
\dot{N} = \frac{1}{k_B T} \left( \frac{\pi \bar{p} a^4}{8 \eta \ell} + \frac{8}{3} \sqrt{\frac{\pi a^3}{2 \ell v}} \left( 1 + \frac{2av\bar{p}}{\eta} \right) \right) (p_1 - p_2), \tag{2.10} 
\]

where \( v = \sqrt{m/(k_B T)} \), and \( m \) is the mass of a single gas molecule.

In the molecular flow regime, the flow rate through a channel with circular cross section is given by \[25\]
\[ 
\dot{N} = \frac{1}{k_B T} \frac{8}{3} \sqrt{\frac{\pi a^3}{2 \ell v}} (p_1 - p_2). \tag{2.11} 
\]

It is seen that for molecular flow, the flow conductance is independent of the pressure.

The pressure dependence of the viscosity is negligible for both liquids and gases \[29\]. The viscosity of a gas increases with temperature, and the temperature dependence can be approximated using Sutherland’s law \[30\]
\[ 
\eta = \eta_0 \left( \frac{T}{T_0} \right)^{\frac{3}{2}} \frac{T_0 + S}{T + S}, \tag{2.12} 
\]

where \( \eta_0 \) is the viscosity at the reference temperature \( T_0 \), and \( S \) is a parameter characteristic for the gas. In general, Sutherland’s law can be applied in a wide temperature range. For oxygen, Eq. (2.12) is accurate within 2% in the temperature range 190-2000 K, and the appropriate temperature range is comparable for many other relevant gases. Sutherland’s law is strictly valid only for a single component substance. For a gas mixture consisting of markedly different species, the mixture viscosity varies strongly with species concentration \[30\].

The analytical expressions given here are important when designing the microchannel system, since the gas flow through the microreactor is an essential parameter for the device. For instance, these equations are useful for predicting residence times and the pressure distribution in the microchannel system. Furthermore, an understanding of the gas flow in the microchannel system is imperative for dimensioning mixing channels and flow-limiting capillaries.

## 2.2 Microreactor design

In this section, the fundamental microchannel system design is considered. The fundamental requirements to a continuous-flow microreactor for obtaining high sensitivity and low response time are discussed. The design issues considered here serve to motivate the microreactor designs presented in chapter 3 and 5.

### 2.2.1 Microreactor sensitivity

One of the most important requirements of the microreactors considered in this thesis is that they must facilitate detection of gas species that are produced at a low rate (low total...
number of molecules per unit time). The effect of microchannel design on the sensitivity
on the sensitivity
can be examined with the following quantitative considerations. Consider a continuous
flow experiment with a gas phase reaction, where the aim is to measure the catalytic ac-
tivity of a low-area catalyst with a total number of active surface sites $N_{\text{sit}}$. Assume steady
state conditions and that the reaction is reaction rate controlled with low conversion. Reaction
rate control is a realistic assumption, since the active surface area is low. The absolute
reaction rate of product formation $\dot{N}_P$ is then given by

$$\dot{N}_P = fN_{\text{sit}}, \quad (2.13)$$

where $f$ is the turn-over frequency, the absolute number of products formed per surface
site per unit time. Since the reaction is reaction rate controlled, $f$ is independent of the total
gas flow rate through the catalyst bed, as long as the pressure is constant. The criterion for
detection of catalytic activity depends on the sensitivity $\chi_i$ of the gas composition analysis.
$\chi_i$ is defined as the minimum fraction of molecules of species $i$ in the gas required to obtain
detection. Let $\dot{N}_{\text{gat}}$ be the total number of gas molecules entering the gas analysis tool per
unit time. Then, the criterion for detection is

$$\frac{\alpha\dot{N}_P}{\dot{N}_{\text{gat}}} \geq \chi_P, \quad (2.14)$$

where $\alpha$ is the fraction of the formed products that eventually enters the gas analysis tool
($0 \leq \alpha \leq 1$). Unless the entire reaction zone gas flow is directed to the gas analysis tool,
$\alpha$ will be less than one. Likewise, back-diffusion of products from the reaction zone into
the inlet channel will reduce the value of $\alpha$.

By insertion of Eq. (2.13) into Eq. (2.14) and rearranging, the criterion for detection
can be expressed as

$$N_{\text{sit}} \geq \frac{\chi_P\dot{N}_{\text{gat}}}{\alpha f}. \quad (2.15)$$

It is clear that a value of $\alpha$ close to one will improve the sensitivity. It also appears
from Eq. (2.15) that a low value of $\dot{N}_{\text{gat}}$ is favorable for the purpose of obtaining high
sensitivity. In this project, a quadropole mass spectrometer (QMS) is used for gas com-
position analysis. When the microreactor is used in gas phase reactions, the product gas
is fed directly to the QMS. In liquid phase reactions, a carrier gas streams by a confined
liquid droplet and is subsequently fed to the QMS. In this case, reaction products diffuse
from the interior of the droplet out into the gas phase, and the products can thus be de-
tected with QMS. With the QMS, sensitive gas composition analysis can be a carried out
with a flow rate down to around $1 \times 10^{14}$ molecules s$^{-1}$. The reaction zone pressure is
of the order of magnitude of 1 bar, while the QMS pressure is at vacuum level. Since the
flow rate into the QMS must be limited to about $1 \times 10^{14}$ molecules s$^{-1}$, the catalyst bed
must be connected to the QMS through a capillary with a low flow conductance.

For a specific experiment, the minimum number of active sites $N_{\text{sit}}$ required for de-
tection of catalytic activity can be estimated from Eq. (2.15). Suppose that $\dot{N}_{\text{gat}} = 1 \times
10^{14}$ molecules s$^{-1}$, and that $\chi_P = 5 \times 10^{-6}$, which is a realistic value for the sensitivity of
a QMS. Furthermore, assume that the turn-over frequency $f$ is $10$ s$^{-1}$, which is a typical
value for e.g. many oxidation reactions. The value of $\alpha$ is assumed to be 1 to consider an ideal situation, where the entire reaction zone gas flow is directed to the QMS, and where back-diffusion has been eliminated. With these values, Eq. (2.15) yields $N_{\text{sit}} \geq 50 \times 10^6$ as the criterion for detection. Suppose that the aim is to measure the catalytic activity of size selected nanoparticles with a diameter of 10 nm. The number of surface sites on a nanoparticle of this size is approximately 2500, yielding a minimum of $20 \times 10^3$ nanoparticles for detection of catalytic activity. This number of nanoparticles would be convenient both with respect to deposition time and suppression of sintering.

2.2.2 Constraints on microreactor system

The results from the preceding section show that potentially high microreactor sensitivity is obtainable with a QMS. It is also clear that the highest sensitivity is obtained when: (1) the entire reaction zone gas flow is directed to the QMS, so that $\alpha \approx 1$. (2) The flow rate into the QMS is kept low, while still being within the range of optimal detection. If these requirements are satisfied, then the gas flow rate through the reaction zone $\dot{N}_{\text{rz}}$ is given by $\dot{N}_{\text{rz}} = N_{\text{gat}} \approx 1 \times 10^{14}$ molecules s$^{-1}$. This is a comparatively low flow rate. Consequently, the reaction zone must have a relatively small volume to ensure a sufficiently low residence time of the gas in the catalyst bed. As an example, suppose that for practical reasons, the maximal acceptable residence time is 1 min. With a value of $1 \times 10^{14}$ molecules s$^{-1}$ for the reaction zone flow rate, and with atmospheric pressure and room temperature in the catalyst bed, this entails a maximal volume of around 250 nl.

These considerations demonstrate the value of microreactors when measuring catalytic activity in reactions with low absolute reaction rates. A reaction zone of very small volume is necessary. In addition, a capillary with a low flow conductance is required for connecting a catalyst bed at atmospheric pressure to a QMS at vacuum pressure. Microtechnology can provide both of these features in one compact device. In its simplest version, the role of the microreactor is to provide a micrometer-sized reaction zone for containing the reaction and a micrometer-sized flow limiting capillary, which feeds the QMS with gas at a low flow rate.

It has been demonstrated that the flow rate through the reaction zone should be low, preferably at the order of $10^{14}$ molecules s$^{-1}$. It will now be argued that this feature places an additional constraint on the microchannel system. Firstly, such a low flow rate is difficult to control with off-the-shelf mass flow controllers (MFCs). In general, only gas flows of the order of $10^{18}$ molecules s$^{-1}$ or higher can be readily controlled with off-the-shelf MFCs. Secondly, the volume of the exterior gas supply system connecting the microreactor to the experimental setup is much larger than the volume of the microchannel system itself. When changing the composition of the gas entering the microchannels one therefore has to wait for the old gas to be fully washed away from the exterior tubing by the new gas. Until then, the composition of the gas entering the reactor does not resemble the one specified by the user. Thus, a relatively high gas flow is required to enter the microreactor to ensure a short gas residence time in the exterior tubing. It follows that, in addition to the low-flow channels, the microchannel system must include a main flow channel which carries a much higher gas flow. This is necessary to ensure a practical
time-scale for changes of the gas mixtures and in order to control the gas flows into the microreactor with MFCs.

The preceding discussion elucidates the constraints on the microreactor system. The concept of continuous flow operation and the requirements of high sensitivity and high space velocity place the following demands on the microreactor design [12]: (1) the fluid flow rate through the catalyst bed must be small, to avoid unnecessary dilution of products. (2) Because of the low flow rate, the reaction zone volume must be small to ensure a relatively short gas residence time. (3) As another consequence of the low flow rate, the leak rate between the microchannel system and the surroundings must be low. If gases leak into or out of the microchannel system at rates comparable to the reaction zone gas flow it could seriously complicate interpretation of experimental data. (4) In many cases, the area of the microchannel walls will be large compared to the active catalyst surface area, implying that the wall material must be inert. (5) The microchannel system must include a main flow channel, which carries a relatively high gas flow. (6) The detection method used for measuring product conversion must be compatible with the low flow rate. QMS detection satisfies this last requirement.

### 2.2.3 Generic microchannel system

Based on the analyses in section 2.2.1 and 2.2.2, the basic microreactor concept employed in this project will now be presented. The basic idea with the microchannel system design is to provide a reaction zone with a small volume and to direct the entire reaction zone gas flow to a QMS, as described in section 2.2.2. The reaction zone is connected to the QMS through a lateral, narrow capillary with a low flow conductance. This capillary acts as a flow limiting orifice.

Silicon and Pyrex have been chosen as the reactor materials. These materials meet the requirement of being catalytically inactive for the reactions of interest, and silicon is widely used as a microreactor material [31]. In addition, a wide range of well established fabrication techniques is available for defining microstructures in silicon. Due to the pivotal role of silicon in the microelectronics industry, a large number of very useful manufacturing processes has been developed for this material. Another strong argument for employing silicon and Pyrex in the microreactor system is that these two materials can be bonded hermetically to each other using anodic bonding (see section 2.3). This sealing method is especially well-suited for the microreactor system, since it can produce a tight bonding between surfaces which are not perfectly clean. The microreactors considered in this thesis basically consist of a microchannel system which has been etched in a silicon chip using DRIE and RIE. All the microchannels have rectangular cross sections. The chip has dimensions of $16 \times 20 \text{ mm}^2 \times 350 \mu\text{m}$ (see Fig. 2.4). The entire surface of the silicon chip is thermally oxidized with an oxide thickness of 50 nm. The oxide provides electrical insulation of the silicon. This is convenient when electrical components such as electrodes for electrolysis are integrated in the device. The oxide also serves another purpose. If catalytic, metallic nanoparticles were deposited directly on the surface of bulk silicon, the metal could mix with the silicon and form a silicide. This potential problem is avoided by virtue of the oxide layer which acts as an effective barrier between metal nanoparticles and
2.2 Microreactor design

Figure 2.4: Photograph of one of the microreactors fabricated during the project. The device consists of a microchannel system which has been etched in a silicon chip using RIE and DRIE. The silicon chip has dimensions of $16 \times 20 \text{ mm}^2 \times 350 \mu\text{m}$. A blank Pyrex lid with dimensions of $16 \times 20 \text{ mm}^2 \times 500 \mu\text{m}$ is bonded to the chip for the purpose of sealing the microchannel system. The microreactor shown in the photograph is designed for gas phase reactions and is discussed in more detail in chapter 3.

the bulk silicon. The microreactors are intended for reaction zone pressures in the range of 0.1-5.0 bar, and the channel system is sealed with a Pyrex lid by anodic bonding.

The basic topology of the microchannel system is sketched in Fig. 2.5. The chip includes one or two inlet holes, through which reactant gas mixtures can be introduced into the channel system. In addition, two outlets (O1 and O2) are included in the chip. The inlets and outlets all consist of 600 $\mu\text{m}$ diameter holes which extend from the front side to the back of the chip. The inlets are connected to a main flow channel with a high flow conductance, and the main flow channel connects to O1. The reactant gas mixture enters the chip through the inlets and leaves the microreactor through O1. This gas flow is typically on the order of 10 Nml min$^{-1}$ ($4.1 \times 10^{18}$ molecules s$^{-1}$). The relatively high main flow ensures that the gas residence time in the exterior tubing is sufficiently low, and that the gas flow entering the chip can be controlled with standard MFCs, as described in section 2.2.2.

The channel system contains a low-volume reaction chamber, where the chemical reaction occurs. In experiments, the catalyst is contained within this chamber. The reaction chamber is connected to O2 through a flow-limiting capillary and to the main flow channel through another channel, which has a much higher flow conductance than the capillary. The purpose of the latter channel is to limit diffusion mass transfer between the reaction zone and the main flow channel. Gas flows from the main flow channel into the reaction chamber and proceeds to O2. This gas flow is typically on the order
Figure 2.5: Simplified sketch of the generic microchannel system topology. Dashed arrows represent gas flows. Gas is introduced into the chip through the inlet hole, and a main flow channel with a high flow conductance connects the inlet to O1, where gas is vented to the atmosphere. A small fraction of the gas in the main flow channel enters the reaction chamber and proceeds through the capillary to O2. The gas flow to O2 subsequently continues to a QMS, which analyzes the gas composition. The low flow part of the channel system is colored grey while the high flow part is colored white. For simplicity, only a single inlet is shown in the sketch, even though many of the reactors fabricated in the project contained two inlets.

Thus, the gas flow through the reaction chamber is only around 0.01 – 0.10% of the main flow, because the flow conductance of the capillary is much lower than that of the main flow channel. O2 is connected directly to a QMS which analyzes the composition of the gas leaving the reaction chamber. Thus, the entire gas flow through the reaction chamber, and consequently almost all reaction products, enter this QMS. Only reaction products which might back diffuse from the reaction chamber into the main flow channel will elude the QMS.

In the experimental setup, the absolute pressure at O1 can be varied in the range of 0.1-5.0 bar. The absolute pressure at O2 is at vacuum level, since this outlet is connected to the QMS. It follows that there is a pressure difference of the order of 1 bar across the system. Since the flow conductance of the capillary is much lower than the conductance of any other part of the channel system, most of the pressure drop occurs across the capillary. Consequently, the pressure in the reaction chamber and in the main flow channel are expected to be close to the controlled pressure at O1.

In the main flow channel, continuum flow will in general be expected due to the relatively high pressure and large cross sectional dimensions. Everywhere the flow is in the continuum regime, it is also laminar, due to the μm-scale of the cross sections which results in Reynold’s numbers well below 1000. In the low flow part of the channel system, continuum flow can not in general be assumed, and the flow regime will depend on the exact dimensions of the channels. Especially in the capillary and at O2, where the pressure
is reduced to vacuum level, the possibility of noncontinuum flow regimes must be taken into account.

In summary, reactant gases are introduced into the reactor through one or two inlets. The reactant gas mixture flows through the main flow channel to O1, where it is vented to the atmosphere. However, around 0.01 – 0.10% of the main flow channel gas flow proceeds to the reaction chamber, where products can form under influence of the catalyst. The resulting gas mixture flows from the reaction chamber through the capillary and enters the QMS, where the gas composition is analyzed.

In the following, the reaction chamber geometry will be considered. It will be argued that a circular reaction chamber with a large floor area is convenient for the intended applications. A large floor area increases the amount of catalyst which can fit at the floor of the reaction chamber for a given density. This is favorable for the purpose of obtaining a reasonably high reaction rate when the turnover frequency is low, or when a low catalyst density is required to avoid sintering. A circular shape is an advantage since it makes confinement of the catalyst deposition to the reaction chamber easier than it would be, if for instance a long, narrow meander geometry of the same large area were used. When depositing metal clusters from a magnetron sputtering cluster source, a large, circular shape makes it fairly easy to align a shadow mask. When depositing a catalyst manually with a pipette, a high area and circular shape also ease the process. In addition, with a circular design liquid catalyst suspensions deposited in the reactor form a relatively uniform loading. Finally, a circular shape allows easy use of the “locally cooled anodic bonding” method, which is described in chapter 4. This bonding method is very useful for catalysts, such as gold clusters, which are likely to sinter at elevated temperatures [32].

It has been argued that a circular reaction chamber floor with large diameter is desirable. The possibilities of integrating such a reaction chamber in the microreactor design are investigated in section 2.3.

2.3 Anodic bonding

As outlined above, the reaction chamber should preferably have a circular floor with a large diameter. As mentioned in section 2.2.2, the reaction chamber should also have a low volume. Reconciliation of these two requirements entails a very shallow chamber. In the following, these constraints are further discussed in the context of the chip bonding process.

2.3.1 Basic concepts

As described in section 2.2.3, the microchannel system is sealed with a Pyrex glass lid using anodic bonding [33]. Anodic bonding is a method for obtaining strong, leak-tight bonds between an ion-conductive glass on one side and a metal, a metallic alloy or a semiconductor on the other side. Even though this bonding method is compatible with several materials, it is almost exclusively applied to the bonding of silicon to Pyrex glass [34].

A conventional anodic bonding setup is sketched in Fig. 2.6. The basic principle of this bonding method is to place two wafers, typically a silicon and a Pyrex wafer, on top of each
2. Generic microreactor design

Figure 2.6: Schematic picture of experimental setup for anodic bonding with point cathode electrode. The Pyrex and silicon are heated to an elevated temperature with the hotplate while simultaneously applying a potential between the hot plate and the cathode. After a period of time, a permanent bond between the Pyrex and silicon is formed.

other, surface to surface. A voltage is applied across the wafer stack while heating it to an elevated temperature. The potential of the Pyrex wafer must be negative with respect to the silicon. Typically, the applied voltage is in the range of 100-1500 V, and the temperature is between 250 and 500 °C. After a period of time, a permanent hermetic bond between the wafers is obtained, and the voltage and heating can be switched off. The required bonding time depends on the voltage, temperature and the size of the wafers. Typically, bonding is obtained within 15-30 min. Fig. 2.7 shows a photograph of a microreactor being sealed with anodic bonding.

The bonding mechanism can be understood as follows. When the two wafers are first placed on top of each other, the surfaces will not be in intimate contact over the whole interface, since air gaps will be present between the wafers. Typically, such air gaps are at most a few micrometers thick. The Pyrex glass contains sodium ions which become mobile at the elevated temperatures used in the bonding process. During anodic bonding, these mobile ions migrate to the cathode under influence of the applied electric field, leaving behind a negatively charged region in the Pyrex adjacent to the silicon (see Fig. 2.8). The silicon surface becomes positively charged, and due to the polarization of the Pyrex, almost the entire voltage difference falls across the air gaps at the Pyrex-silicon interface. Consequently, the two surfaces are attracted towards each other by a strong electrostatic force [35], and intimate contact is established over the entire interface. The formation of intimate contact between the silicon and Pyrex surfaces and a sodium depletion layer within the glass cannot by themselves explain the high bond strength obtained with anodic bonding. It is generally believed that a chemical reaction occurs at the interface, forming a thin oxide layer which is responsible for the hermeticity and high strength of the bond [34,36–40]. For silicon-Pyrex bonding, the reactions believed to take place at the interface are

\[ \text{Si} + \text{O}_2 \rightarrow \text{SiO}_2, \]

and

\[ \text{Si} + \text{O}_2 \rightarrow \text{SiO}_2. \]
2.3 Anodic bonding

Figure 2.7: Photographs of a silicon microreactor being sealed with a Pyrex lid using a conventional anodic bonding setup. The silicon surface contains a microchannel system with depths of 3 μm (and of 250 μm in a small part of the system). The left picture shows the stack after a short bonding time. Newton rings are clearly visible in the areas where bonding has not yet occurred. The picture to the right shows the same stack at a later time. A larger part of the interface has now bonded, and the area with Newton rings is smaller. Bonding is complete when the Newton rings have disappeared all over the interface. Note how the shallow microchannel system is clearly visible in the bonded areas.

Figure 2.8: Illustration of sodium ion migration during anodic bonding of silicon to Pyrex. The sodium ions become mobile because of the elevated temperature and migrate to the cathode. A negatively charged layer is left behind adjacent to the silicon causing a strong electrostatic attraction between the two materials at the silicon-Pyrex interface.
Figure 2.9: Cavity collapse during anodic bonding. Because of the low depth-to-width ratio of the groove, the glass and silicon get into intimate contact under influence of the strong electrostatic attraction. Attractive surface forces quickly cause the entire cavity to collapse, permanently bonding the glass to the floor of the groove.

\[
\text{Si} + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2 + 2\text{H}_2. \tag{2.17}
\]

There is no widely accepted consensus about the sources of oxygen and water in these reactions [34]. The water could originate from hydroxyl groups present on the wafer surfaces or from water being adsorbed on the wafer surfaces. The thickness of the silicon oxide layer at the interface is generally believed to be 10 – 12 nm.

The quality of the final bond depends on the thermal mismatch between the two wafers in terms of the coefficient of thermal expansion. One of the reasons for the popularity of the silicon-Pyrex configuration is that the thermal mismatch between these two materials is relatively small (less than \(1 \times 10^{-6} \text{ K}^{-1}\)) in the range of 0-500 °C. The main advantages of anodic bonding compared to e.g. fusion bonding are that it can tolerate rougher surfaces and does not require an ultraclean environment. The most important disadvantage is that the wafers must be heated to relatively high temperatures in order for the ions in the glass to become mobile [41].

### 2.3.2 Cavity collapse

When performing anodic bonding with a silicon wafer containing grooves with low depth-to-width ratios, there is a risk that the glass and the floor of the grooves might get into intimate contact due to the electrostatic attraction. If this happens, the attractive forces will quickly cause the entire groove to collapse, permanently bonding the glass to the floor of the groove (see Fig. 2.9). Such a collapse will be detrimental to device performance for many applications. In general it is observed that for a given depth there is a critical width of the groove above which anodic bonding causes the groove to collapse [34,42–45].

In the context of the microreactor design, cavity collapse during anodic bonding is a potential problem, especially for the reaction chamber, for which a low height and a large diameter are desirable. Thus, there is a need for determining the maximum diameter for which cavity collapse can be avoided with a given depth of the cavity. A number of studies of the conditions for cavity collapse during anodic bonding has been reported in literature. Plaza et al. [42, 43] studied the conditions for collapse of RIE formed grooves in silicon. This study aimed at investigating the relation between the depth and the critical width above which the cavity collapses. The glass used was 1 mm thick and of type Hoya SD-2, the bonding was performed at 400 °C and 1000 V, and the cavity depths ranged
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from 80 to 370 nm. It was clear from the experimental data that for circular grooves the critical diameter as a function of the depth fit well with a power function. Thus, the critical diameter was directly proportional to the depth to the power of 1.43, with a proportionality constant of $850 \times 10^3 \, \text{m}^{-0.43}$. Likewise, for long channels the critical width was directly proportional to the depth to the power of 1.32 with a proportionality constant of $91 \times 10^3 \, \text{m}^{-0.32}$ [34, 42, 43]. Also in the case of long channels the power function fit was in good agreement with the experimental data. Furthermore, Plaza et al. reported that reducing the applied voltage did not seem to affect the critical width although it increased the dispersion of results across the wafer. Finally, it was reported that the electrostatic pressure during bonding decreased greatly when the bonding temperature was reduced. Based on calculations of the electric field and the elasticity of the materials involved, Shih et al. [44] developed a theoretical model for the critical width of long channels with rectangular cross sections. According to this model, the critical width of a channel should be proportional to the depth to the third power and inversely proportional to the voltage across the cavity to the second power. To investigate the conditions for cavity collapse experimentally, Shih et al. dry etched long microchannels with different depth-to-width ratios in silicon wafers. Subsequently, the structured silicon wafers were bonded to 500 μm thick Pyrex wafers using anodic bonding at 350−450 °C. For a bonding voltage of 1022 V and groove depths in the range of 48−132 nm the best power function fit to the experimental data suggested that the critical diameter was directly proportional to the depth to the power of 2.42. The corresponding proportionality constant was $7.3 \times 10^{12} \, \text{m}^{-1.42}$ [34, 44]. However, these experimental data exhibited a substantial amount of scatter and deviated markedly from the power function fit. In addition, the agreement between the theoretical model and the presented experimental data was less than perfect, as evident from the experimentally found exponent of 2.42 in contrast to the exponent of 3.00 predicted by the model. Mao et al. [45] presented an experimental study of the critical width of long microchannels etched in silicon using RIE and bonded to 500 μm thick Pyrex glass using anodic bonding at 350 °C and 800 V. After etching of the channels but prior to bonding, a 390 nm thick oxide layer was grown on the silicon wafers using thermal oxidation. The experimental data obtained in this work suggested that for depths in the range of 20−180 nm, the critical diameter and the depth exhibited a linear relationship. Thus the critical diameter was approximately proportional to the depth to the power of 1.0 with a proportionality constant of 250.

In general the experimental data reported in literature lack agreement in detail with the theoretical predictions by Shih et al. [34, 45]. No widely accepted theoretical model exists for the conditions for cavity collapse during anodic bonding. Thus, there is a need for further work in this area in which channel collapse should be monitored systematically as a function of the bonding parameters.

In the project presented in this dissertation, a series of experiments was carried out to investigate the conditions for collapse of circular cavities during anodic bonding. The aim was to determine appropriate dimensions for the reaction chamber in the microreactor. Grooves with varying diameters and depths were etched in silicon wafers using UV photolithography and RIE. Subsequently, the silicon wafers were bonded to Pyrex wafers using anodic bonding, and cavity collapse was monitored as a function of the depth
and diameter. Two different photolithographic masks were used in these experiments, as shown in Fig. 2.11 and Fig. 2.12. The first mask (mask 1) contained regular circles, with no supporting structures, of diameters of 1, 2, 3, 5, 7, and 10 mm, respectively. Mask 1 also contained similar circles with 20 \( \mu \text{m} \) diameter circular support pillars distributed inside the cavity. The purpose of these silicon pillars was to support the Pyrex lid during bonding and thus prevent a cavity collapse. The circles with support structures had diameters of 3, 5, 7, and 10 mm, respectively. The second mask (mask 2) design aimed at further investigating the effect of silicon support pillars. This mask had circles with diameters of 5, 6, 7, 8, 9, and 10 mm, respectively, all of them containing support pillars in a hexagonal pattern. For each diameter, the mask included cavities with 200 \( \mu \text{m} \) pillars spaced 1 mm apart, 200 \( \mu \text{m} \) pillars spaced 2.25 mm apart, and 100 \( \mu \text{m} \) pillars spaced 1 mm apart, respectively. The fabrication sequence is outlined in Fig. 2.10 and is described in the following.

1. The starting point is a 525 \( \mu \text{m} \) thick 4” single side polished (100) silicon wafer. First, the front of the wafer is spincoated with a 1.5 \( \mu \text{m} \) thick AZ5214 photoresist layer that is subsequently patterned with UV lithography, using either mask 1 or 2.

2. The resist pattern is etched using RIE with photoresist as the masking material. The etch depth is varied from wafer to wafer by varying the etching time. After the etch, the photoresist layer is removed using acetone.

3. The Pyrex wafer, which has a thickness of 500 \( \mu \text{m} \), is cleaned for 10 min. at 80 °C in a 98%\text{mass} mixture of sulphuric acid in water mixed with ammonium sulfate powder. Subsequently, the silicon and the Pyrex wafers are bonded to each other using anodic bonding with a bonding temperature of 250 °C, a bonding voltage of 400 V and a bonding time of around 15 min. An EV Group 520 Hot Embosser bonding tool is used to carry out the anodic bonding.
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Figure 2.11: Layout of test structures on mask 1 for cavity collapse experiments. The wafer is etched in the black areas. The grooves in the uppermost row contain no support pillars, whereas the grooves in the two lowest rows contain 20 μm diameter circular support pillars distributed over the trench. For the purpose of making the pillars visible in the figure the diameter of the pillars has been greatly exaggerated.

Figure 2.12: Layout of test structures on mask 2 for cavity collapse experiments. The wafer is etched in the black areas. The grooves in this particular test structure contain 200 μm diameter circular support pillars spaced 1.00 mm apart. The mask also contains two other similar test structures with 200 μm pillars spaced 2.25 mm apart, and 100 μm pillars spaced 1.00 mm apart, respectively (not shown in the figure). The pillars are shown with their actual size.
After bonding was complete, the etched cavities were inspected with the naked eye and in an optical microscope to conclude which cavities had collapsed. In this way it is relatively straightforward to conclude whether a cavity has collapsed, as illustrated in Fig. 2.13. In case the groove has not collapsed, interference patterns are apparent when looking at the cavity through the Pyrex, while a collapsed cavity has a grey, dull color when observed in the same way.

Experimental results for wafers fabricated using mask 1 are plotted in Fig. 2.14. The data presented in this figure were obtained with open, circular cavities which did not contain any additional features inside them, thus no silicon pillars or other supporting structures were present inside these cavities. The highest diameter for which no cavity collapses occurred across the entire wafer is plotted as a function of the depth. It appears from Fig. 2.14 that the critical diameter increases with the etch depth, as expected.

Similar to other studies of cavity collapse reported in literature [34, 44], the experimental data shown in Fig. 2.14 were fitted with a power function of the form

\[ d_c = b_1 h^{b_2}, \]  

(2.18)

where \( d_c \) is the critical diameter, \( h \) is the depth of the cavity, and \( b_1 \) and \( b_2 \) are fitting parameters. The fitted values of the parameters were \( b_1 = 3275 \, \text{m}^{-0.080} \) and \( b_2 = 1.080 \), and it follows that the critical diameter increases approximately linearly with the depth. The power function fit is plotted in Fig. 2.14 along with the experimental data. It should be kept in mind that only six different groove diameters were represented on the photolithographic mask used in these experiments. A higher number of different diameters would have given a more accurate determination of the critical width for a given depth and would also have resulted in somewhat different fitting parameters. In spite of this, for the bonding parameters used in these experiments (250 °C, 400 V), Fig. 2.14 gives useful information about the maximum diameter for a given depth. Based on the experimental results reported by Plaza et al. [42, 43] it is believed that the relation between depth and critical diameter presented in Fig. 2.14 is also valid at higher voltages, as long as the bonding temperature is approximately 250 °C. It was characteristic for all test wafers fabricated using mask 1 that the presence of the 20 μm diameter support pillars did not increase the critical diameter (not shown in Fig. 2.14). Thus, in no case did cavities supported by 20 μm diameter pillars have a higher critical diameter across the entire wafer than corresponding cavities without pillars.

Four different test wafers with different etch depths were fabricated using mask 2. The results obtained with this mask are summarized in Table 2.1. Comparison between Table 2.1 and Fig. 2.14 suggests that it is possible to dramatically increase the critical diameter by including support pillars in the groove, which is one of the main findings of the experiments described in this section. It appears from Table 2.1 that groove diameter and depth as well as separation distance between pillars have a substantial influence on the occurrence of cavity collapse. The experimental data also indicate that the pillar diameter is decisive for how effectively the pillars act to prevent cavity collapse. A pillar diameter of 20 μm was not found to yield any significant increase in the critical diameter, and a diameter of 100 μm was found to be considerably less effective than than a diameter of 200 μm. The importance of pillar diameter might indicate that the conditions for cavity
2.3 Anodic bonding

Figure 2.13: Photograph of test wafer for investigating the conditions for cavity collapse during anodic bonding. The test structures on the wafer were made with mask 1, which is illustrated in Fig. 2.11. Areas where silicon and glass are bonded have a dark, dull color, whereas unbonded areas appear bright with interference patterns. It is seen that wide structures have collapsed, while narrow structures have survived. Collapsed grooves have a narrow unbonded region along the rim, where the silicon and glass are not in contact. In this particular wafer the grooves have a depth of 4.1 μm.
2. Generic microreactor design

2.3.3 Reaction chamber design

Based on the results from these experiments, appropriate dimensions were determined for the reaction chamber inside the microreactor. In the generic microreactor design, it was decided to fabricate reaction chambers with a diameter of 1.00 cm and a depth of about 3 μm. It was furthermore decided to design the chambers with 200 μm circular silicon support pillars separated 1 mm apart in a hexagonal pattern. Thus, the layout of the reaction chamber was exactly identical to the largest test groove shown in Fig. 2.12 (the test groove to the lower right in the figure). Considering the results from Table 2.1, chambers with such dimensions should be unlikely to collapse. These dimensions also meet the requirements of a large floor area (79 mm²) and a low volume (240 nl), as mentioned in section 2.2.3. Table 2.1 suggests that chambers even shallower than 3 μm should be possible with a diameter of 1.00 cm; however, a depth of 3 μm was believed to be favorable for several reasons. Firstly, it was deemed suitable to include a safety margin in the design to eliminate the risk of cavity collapse during bonding under conditions different from those of the test experiments, e.g. at higher bonding temperatures. In addition, it can often be expedient to form part of the microchannel system in the same etching step where the reaction chamber is formed, and a depth of 3 μm makes it possible to form relatively wide channels with no support pillars without any risk of collapse. In addition, as described in section 2.4.2, a lower depth could make it difficult to achieve a low pressure difference be-

Figure 2.14: Data from experiments with cavity collapse during anodic bonding. The highest diameter for which no cavity collapses occurred across the entire wafer is plotted as a function of depth. The data were obtained with open, circular grooves without any supporting pillars. Circles represent experimental data points, and the dashed curve is the best power function fit.

collapse are not only governed by the elastic properties of the materials but also by viscous behavior of the Pyrex glass.
2.4 Mass transfer in microchannel system

This section concerns mass transfer in the low flow part of the channel system (see Fig. 2.5). Particular attention is given to the channel connecting the main flow channel and the reaction chamber. In the following, this channel will be referred to as the “inlet channel” (it should not be confused with the inlet holes which connect the chip to the exterior tubing). As mentioned in section 2.2.3 the main purpose of the inlet channel is to limit diffusion mass transfer between the main flow channel and the reaction chamber. Limitation of diffusion mass transfer in the low flow channels is desirable for two reasons. Firstly, back-diffusion from the reaction zone to the main flow channel will reduce the sensitivity, as discussed in section 2.2.1. Secondly, diffusion mass transfer will complicate determination of reaction rates.

This section starts with a brief review of the theory of mass transfer in a gas mixture. Subsequently, the motivation for limiting diffusion in the microchannel system is discussed in more detail. The section concludes with a quantitative analysis of mass transfer in the microreactor for the purpose of providing guidelines for microchannel system design.

<table>
<thead>
<tr>
<th>Etch depth (μm)</th>
<th>Pillar diameter: 200 μm</th>
<th>Pillar diameter: 100 μm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pillar separation: 1 mm</td>
<td>Pillar separation: 1 mm</td>
</tr>
<tr>
<td>1.3</td>
<td>10</td>
<td>∆</td>
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<tr>
<td>1.6</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>1.7</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>1.8</td>
<td>10</td>
<td>6</td>
</tr>
</tbody>
</table>

Table 2.1: Outcome of experiments with cavity collapse during anodic bonding for circular cavities with circular silicon support pillars. For each of the three different pillar configurations (pillar diameter and separation distance) different grooves with diameters of 5, 6, 7, 8, 9, and 10 mm, respectively, were fabricated. For each combination of etch depth and pillar configuration, the maximum diameter, for which no cavities collapsed across the entire wafer, is stated in units of mm. In the table, a “∆” signifies that for the given pillar configuration and etch depth, all cavities collapsed.
2.4.1 Mass transfer in a gas mixture

In the following, we consider a gas mixture consisting of two or more species. The total flux of species \( i \) within the mixture \( \dot{N}''_i \) is defined as the total number of \( i \) molecules that is transferred per unit time and per unit area perpendicular to the area of transfer. The total flux is given by

\[
\dot{N}''_i (\mathbf{r}) = -c(\mathbf{r})D_i(\mathbf{r})\nabla \left[ \frac{c_i(\mathbf{r})}{c(\mathbf{r})} \right] + c_i(\mathbf{r})u(\mathbf{r}),
\]

where \( D_i \) is the diffusion coefficient for species \( i \) in the mixture, \( c \) is the total gas density (total number of gas molecules per unit volume), \( c_i \) is the density of species \( i \) (total number of species \( i \) molecules per unit volume), and \( \mathbf{r} \) is the position. The first and second term on the right side of Eq. (2.19) are the contributions from diffusive and advection mass transfer, respectively.

The diffusion coefficient varies with temperature, pressure, and gas composition. Assuming ideal gas behavior, kinetic theory may be used to show that in restricted but wide ranges of pressure and temperature [46],

\[
D_i \propto p^{-1}T^{3/2}.
\]

If \( c \) is independent of position, Eq. (2.19) reduces to

\[
\dot{N}''_i (\mathbf{r}) = -D_i(\mathbf{r})\nabla c_i(\mathbf{r}) + c_i(\mathbf{r})u(\mathbf{r}).
\]

The results from this section will be used in the following to analyze species mass transfer in the microchannel system.

2.4.2 Species flow rates in microchannel system

In general, experimental use of the microreactor aims at investigating the rate at which species are consumed and/or produced in the reaction chamber and the relation of these rates to the experimental conditions such as the temperature, state of the catalyst, light intensity (in photocatalysis), gas composition, etc. Thus, simple determination of these reaction rates is highly desirable.

By considering a steady state situation and regarding the reaction chamber as a control volume, the rate \( \dot{N}_i,g \) of generation of species \( i \) in the reaction chamber can be determined (see Fig. 2.15). Conservation of species requires that

\[
\dot{N}_i,cap - \dot{N}_i,in = \dot{N}_i,g,
\]

where \( \dot{N}_i,in \) and \( \dot{N}_i,cap \) are the gas flow rates of species \( i \) in the inlet channel and capillary, respectively.

The total capillary flow rate \( \dot{N} \) can be determined from experiment and calibration, and \( \dot{N}_i,cap \) can in general be inferred from knowledge of \( \dot{N} \) and analysis of the QMS data. Furthermore, in the absence of diffusion, determination of \( \dot{N}_i,in \) from Eq. (2.22) would be rather straightforward. The gas composition everywhere in the inlet channel would be the
same as in the reactant gas mixture, and would thus be known in detail. Consequently, with no diffusion, it would be fairly simple to extract the reaction rate \( \dot{N}_{i,g} \) from experimental data. However, the low flow rate through the inlet channel means that diffusion could potentially contribute substantially to the total species mass transfer. As demonstrated in the following, diffusion does complicate the picture, and the gas composition in the inlet channel will in general be different from that of the reactant gas mixture and will also vary with position.

First, consider continuum, laminar gas flow through a long, straight duct with arbitrary, constant cross section and axis parallel to the \( x \)-axis (see Fig. 2.1). Some general properties of species mass transfer in such a duct will now be described. As stated in section 2.1.2, the velocity will be parallel to the \( x \)-axis and can thus be signified \( u_x \). Assume steady state, constant temperature, and no generation of species inside the duct. Also, assume that the pressure drop across the duct is low enough that the pressure can be considered constant. Then the total gas density and all diffusion coefficients are also constant, and the velocity is independent of \( x \). Furthermore, assume that the gas composition is constant across the two ends of the duct (the gas composition is independent of \( y \) and \( z \) on the two planes bounding the duct). Then, to a good approximation, the gas composition of any species \( i \) can be assumed to be independent of \( y \) and \( z \) everywhere within the duct and can thus be signified \( c_i(x) \). In addition, it follows from Eq. (2.21) that with these approximations \( \dot{N}_{i}'' \) is parallel to the \( x \)-axis for any species \( i \) and can thus be designated by its \( x \)-component \( \dot{N}_{i,x}'' \).

In view of Eq. (2.21), the total species flux is given by

\[
\dot{N}_{i,x}''(x,y,z) = -D_i \frac{d c_i}{d x} + u_x(y,z)c_i(x) .
\]  \hspace{1cm} (2.23)

The total species flow rate through the duct is obtained by integrating the flux over a cross section. Thus,
\[ \dot{N}_i = \int_{\Omega} K_{i,x}''(x,y,z) \, da \]
\[ = -D_i A \frac{dc_i}{dx} + c_i(x) \int_{\Omega} u_x(y,z) \, da \]
\[ = -D_i A \frac{dc_i}{dx} + \frac{\dot{N}}{c} c_i(x), \quad (2.24) \]

where, in this context, \( A \) is the cross sectional area.

Since steady state conditions apply, \( \dot{N}_i \) must be independent of \( x \), and it follows that

\[ \frac{d\dot{N}_i}{dx} = 0 \Rightarrow \frac{d^2c_i}{dx^2} - \frac{\dot{N}}{cAD_i} \frac{dc_i}{dx} = 0. \quad (2.25) \]

This is a linear, second order, homogeneous, ordinary differential equation (ODE) with constant coefficients. In the following, this equation will be used to analyze the gas composition in the inlet channel for the purpose of providing guidelines for designing this channel. The assumptions made in the derivation of Eq. (2.25) will in general be justified for gas flow in the inlet channel.

Having derived some general properties for species mass transfer in a duct, we will now return to the particular channel system sketched in Fig. 2.16. First, the flow regime in the inlet channel will be discussed. The criterion for continuum flow is that \( Kn < 0.01 \). The pressure in the inlet channel is at the order of 1 bar. For room temperature and atmospheric pressure the mean free path of atmospheric air is around 70 nm. The corresponding criterion for continuum flow is \( d > 7 \mu m \), where \( d \) is the characteristic cross sectional width. The depth of the inlet channel is 3 \( \mu m \) because this channel is etched in the same RIE process as the reaction chamber. The width of the inlet channel is chosen to be at least 200 \( \mu m \). Thus, it is not straightforward to predict the flow regime in the inlet channel because of the large difference between the height and width of the channel. The hydraulic diameter is around 6 \( \mu m \) which suggests a flow regime close to the transition range between continuum and intermediate. In the following derivations, continuum flow is assumed, which simplifies the analysis considerably. Since the flow is expected to be either in or very close to the continuum regime, this approximation is not expected to invalidate the conclusions in this section.

Consider an experiment where a reactant species R is present in the main flow gas mixture and consumed in the reaction chamber at such a high rate, that the concentration of R is effectively zero inside the reaction chamber. In this situation species R will be transferred to the reaction chamber not only by advection but also by diffusion, because of the concentration difference between the main flow channel and the reaction chamber. Thus the flow of species R into the reaction chamber will be higher than one would expect in the absence of diffusion. Assume that the concentration of species R is \( c_{R,0} \). Thus, the following boundary conditions apply to the concentration of species R in the inlet channel
2.4 Mass transfer in microchannel system

Figure 2.16: Coordinate system for analysis of species mass transfer in inlet channel.

\[ c_R(0) = c_{R,0} \]
\[ c_R(\ell) = 0, \]  \hspace{1cm} (2.26)

where \( \ell \) is the length of the inlet channel. Assume further that in the reactant gas mixture species \( R \) is highly diluted so that \( c_R << c \) everywhere.

The solution to the boundary value problem consisting of the ODE Eq. (2.25) and the boundary conditions Eqs. (2.26) and (2.27) is

\[ c_R(x) = \frac{c_{R,0}}{1 - \exp \left( -\frac{\dot{N} \ell}{cAD_R} \right)} \left[ 1 - \exp \left( -\frac{\dot{N}}{cAD_R} \{\ell - x\} \right) \right], \quad 0 \leq x \leq \ell. \]  \hspace{1cm} (2.28)

The solution is plotted in Fig. 2.17. The corresponding flow rate \( \dot{N}_{R,in} \) of species \( R \) through the inlet channel is given by

\[ \dot{N}_{R,in} = -D_RA \frac{dc_R}{dx} + \frac{\dot{N}}{c} c_R(x) = \frac{c_{R,0}}{1 - \exp \left( -\frac{\dot{N} \ell}{cAD_R} \right)} \]  \hspace{1cm} (2.29)

Ideally, the actual value of \( \dot{N}_{R,in} \) should be approximately equal to \( c_{R,0}c^{-1}\dot{N} \), the flow rate of species \( R \) one would expect in the absence of diffusion. In this case one could make the approximation \( \dot{N}_{R,in} \approx c_{R,0}c^{-1}\dot{N} \) in expressions such as Eq. (2.22) to infer reaction rates. Thus, it is convenient to introduce the ratio \( \beta \) between the flow rate of species \( R \) expected in the absence of diffusion and the actual flow rate. In view of Eq. (2.29), this ratio is given by

\[ \beta = \frac{c_{R,0} \dot{N}}{\dot{N}_{R,in}} = 1 - \exp \left( -\frac{\dot{N} \ell}{cAD_R} \right). \]  \hspace{1cm} (2.30)

\( \beta \) is a figure of merit for the microchannel system which describes how much diffusion contributes to the overall flow of reactants into the reaction zone. It holds that \( 0 < \beta < 1 \), and a value of \( \beta \) close to one eases interpretation of experimental data, since one can then
Figure 2.17: Plot of predicted normalized reactant concentration in inlet channel versus normalized position for different values of the parameter $\gamma = \frac{N_{\ell}}{cAD_R}$. For high and low values of $\gamma$ the mass transfer is dominated by advection and diffusion, respectively.

Assume that $\dot{N}_{R,\text{in}} \approx c_{R,0}^{-1}N$. It is seen that for a constant total flow rate, a long inlet channel with low cross sectional area will act to limit the diffusion.

Having considered the flow of reactants into the reaction chamber, we will now analyze the flow of products out of the reaction chamber. Consider a situation where a product species P is generated inside the reaction chamber in a chemical reaction (see Fig. 2.16). In the microreactor design, the products are supposed to be transferred by advection in the carrier gas to the QMS. However, due to the difference in product concentration between the reaction chamber and the main flow channel, some of the products will diffuse back into the main flow channel in a direction opposite to the overall gas flow. Thus the flow of products into the QMS will be lower than what one would expect in the absence of diffusion. This will limit the sensitivity of the microreactor system as discussed in section 2.2.1. In addition, back diffusion of product species P will make the term $\dot{N}_{P,\text{in}}$ in Eq. (2.22) different from zero (it will be negative), complicating interpretation of experimental data. Ideally, the vast majority of generated products should thus be transferred through the capillary to the QMS.

Assume that the concentration of species P is the same everywhere in the reaction chamber and has the value $c_{P,0}$. A constant product concentration in the reaction chamber is a fairly good approximation, since the low total flow rate gives a relatively long residence time. Thus, the diffusion length for products inside the reaction chamber is expected to exceed the radius of the reaction chamber in most cases. The main flow is so large that all products reaching the main flow channel are expected to be washed away rapidly. It follows that the product concentration can be assumed to be zero in the main flow channel.
Figure 2.18: Plot of predicted normalized product concentration in inlet channel versus normalized position for different values of the parameter $\gamma = \dot{N} \ell (cAD_p)^{-1}$. For high and low values of $\gamma$ the mass transfer is dominated by advection and diffusion, respectively.

Consequently, the following boundary conditions apply to the concentration of products in the inlet channel

\begin{align}
    c_P(0) &= 0 \quad \text{(2.31)} \\
    c_P(\ell) &= c_{P,0}. \quad \text{(2.32)}
\end{align}

Analogous to the analysis of reactant flow, we will assume that in the reaction chamber species $P$ is diluted so that $c_P << c$ everywhere. The solution to the boundary value problem consisting of the ODE Eq. (2.25) and the boundary conditions Eqs. (2.31) and (2.32) is

\begin{align}
    c_P(x) &= \frac{c_{P,0}}{\exp \left( \frac{\dot{N} \ell}{cAD_p} \right) - 1} \left[ \exp \left( \frac{\dot{N} \ell}{cAD_p} x \right) - 1 \right], \quad 0 \leq x \leq \ell. \quad \text{(2.33)}
\end{align}

The solution is plotted in Fig. 2.18. The corresponding flow rate $\dot{N}_{P,\text{in}}$ of species $P$ through the inlet channel is given by

\begin{align}
    \dot{N}_{P,\text{in}} = -D_P A \frac{d c_P}{d x} + \frac{\dot{N}}{c} c_P(x) = -\frac{c_{P,0}}{c} \frac{\dot{N}}{cAD_p} \exp \left( \frac{\dot{N} \ell}{cAD_p} - 1 \right). \quad \text{(2.34)}
\end{align}

Analogous to the reactant flow analysis above, it is useful to introduce a figure of merit which characterizes the contribution of diffusion to the product flow rate. To this end, as in section 2.2.1, the quantity $\alpha$ is defined as the fraction of generated products $P$ that eventually enters the QMS. In view of Eqs. (2.22) and (2.34), this ratio is given by
\[
\alpha = 1 - \frac{-\dot{N}_{P,in}}{-\dot{N}_{P,in} + \dot{N}_{P,cap}} = 1 - \exp \left( -\frac{\dot{N} \ell}{cAD_P} \right),
\]
(2.35)

where it has been assumed that \( \dot{N}_{P,cap} \approx c_P 0 c^{-1} \dot{N} \). This is a good approximation, since, due to the small cross sectional area of the capillary, the gas velocity is very high in the capillary. Consequently, advection completely dominates over diffusion in the capillary.

Comparison between Eqs. (2.30) and (2.35) shows that the expressions for \( \alpha \) and \( \beta \) only differ by the value of the diffusion coefficient \( D_R \) and \( D_P \) for reactants and products, respectively. Most of the reactant and product species relevant to this project have similar diffusion coefficients at given temperature and pressure. Consequently, in most cases \( \alpha \approx \beta \). Hydrogen is an exception since it has an exceptionally high diffusion coefficient, about a factor of five higher than for other relevant species. In the following derivation of guidelines for microchannel system design, \( \alpha \) will be used as a figure of merit describing diffusion limitation.

It is clear from Eq. (2.35) that for a constant total flow rate, a long inlet channel with low cross sectional area will act to suppress back diffusion of products and diffusion of reactants from the main flow to the reaction zone. However, increasing the length and decreasing the cross sectional area of the inlet channel have the inherent disadvantage that the pressure difference across the main flow channel will increase. Consequently, the reaction chamber pressure will differ significantly from the controlled pressure at \( O_1 \). In addition, a large flow resistance between \( O_1 \) and the reaction chamber increases the temperature dependence of the reaction chamber pressure. This is inconvenient since the pressure in the reaction chamber should preferably be constant during temperature ramps. Furthermore, accurate knowledge of the reaction chamber pressure is desirable for interpretation of experimental data. It follows that a compromise must be made: diffusion effects can be limited with a long, narrow inlet channel, but at the expense of less accurate pressure control in the reaction zone. In the following, this trade-off will be analyzed.

The inlet channel, the capillary, and the reaction chamber are all formed in the same etching step, and consequently they will have the same depth \( h \). As explained in section 2.3.2, \( h \approx 3 \mu m \). To ensure that the inlet channel flow resistance is sufficiently lower than that of the capillary, the width of the inlet channel must be much larger than the height, and thus \( w >> h \), where \( w \) is the width of the inlet channel. Since the channel cross section is rectangular, it follows from Eq. (2.9) that to a good approximation

\[
\dot{N} \approx \frac{1}{k_BT} \frac{wh^3}{24\eta\ell} (p_{mf}^2 - p_{rc}^2),
\]
(2.36)

where \( p_{mf} \) and \( p_{rc} \) are the pressures in the main flow channel and in the reaction chamber, respectively. It is clear from this expression that in the exponents of Eq. (2.30) and Eq. (2.35), the factor \( \dot{N}\ell A^{-1} \) can be regarded as independent of \( w \) and \( \ell \) for constant pressures \( p_{mf} \) and \( p_{rc} \). Insertion of Eq. (2.36) into Eq. (2.35) yields

\[
\alpha \approx 1 - \exp \left( -\frac{1}{p_{mf}D_P 24\eta} \frac{h^2}{24\eta} \left[ p_{mf}^2 - p_{rc}^2 \right] \right),
\]
(2.37)
2.4 Mass transfer in microchannel system

Figure 2.19: Plot of the parameter $\alpha$ for realistic values of the physical quantities in Eq. (2.37). The plot shows $\alpha$ as a function of the relative pressure difference $\Delta p/p_{mf}$ between the main flow channel and the reaction chamber. A high value of $\alpha$ indicates efficient suppression of diffusion in the inlet channel.

where the ideal gas law has been used. The pressure in the main flow channel is in the range of 0.1-5.0 bar, and the exact value of this pressure is determined by the specific experiment. It is clear from Eq. (2.37) that for constant pressures the value of $\alpha$ is independent of $\ell$ and $w$ but increases with $h$. This is because the flow conductance depends strongly on the depth. Eq. (2.37) is plotted in Fig. 2.19, which illustrates the trade-off that must be made between diffusion suppression and pressure drop $\Delta p = p_{mf} - p_{rc}$. The plot shows $\alpha$ as a function of the relative pressure difference for $h = 1 - 3 \ \mu\text{m}$, $p_{mf} = 1.00$ bar, $D_P = 13 \ \text{mm}^2 \ \text{s}^{-1}$ (the diffusion coefficient for a dilute mixture of CO$_2$ in air at room temperature and atmospheric pressure), and $\eta = 18 \ \mu\text{Pa} \ \text{s}$ (the viscosity of air at room temperature). It is clear that the trade-off becomes less favorable for more shallow inlet channels.

From Fig. 2.19 it is also seen that for $h = 3 \ \mu\text{m}$, the inlet channel can be designed to yield a relative pressure difference of only 1% and at the same time ensuring that more than 90% of the product molecules are detected. Thus, with this depth it is possible to meet the requirements of low pressure drop and efficient suppression of diffusion. However, it is still imperative to make an informed choice of the inlet channel width and length, since inappropriate dimensions will either lead to a too high pressure drop or too much diffusion. Fig. 2.20 shows a plot of the relative pressure drop and $\alpha$ as a function of the channel length with the same parameters as in Fig. 2.19 and with $h = 3 \ \mu\text{m}$, $w = 200 \ \mu\text{m}$, $\dot{N} = 6 \times 10^{14} \ \text{molecules s}^{-1}$, and $T = 295$ K.

Based on the discussion above, the following procedure is now proposed for designing the inlet channel with reference to suppressing diffusion and maintaining a low pressure drop: (1) first, specify the depth, diffusion coefficient, viscosity, and main flow pressure.
2.5 Experimental setup

All the microreactors fabricated during the project have the same footprint and are designed to fit in a dedicated experimental setup. This experimental arrangement, which can be considered part of the generic microreactor platform, is described in the following.

In order to establish gas connections to the microreactor it is mounted in a fixture, which provides means for a user to operate the microreactor and study the reaction occurring in the reaction chamber. The experimental arrangement is sketched in Fig. 2.21, and a photograph of the setup is shown in Fig. 2.22. The gas handling system, including the fixture, is made from 0.25” stainless steel tubing with welded VCR® (Swagelok) fittings as connections. The gas lines are machined in the interior of the fixture, and tight connections between the steel block and the microreactor are ensured by using Kalrez perfluoroelastomer O-rings.

Since the O-rings are made from an elastomer, a small amount of gas diffusion from the surrounding air into the system is unavoidable, particularly at elevated temperatures. This gives rise to unwanted background signals of O₂ and N₂, complicating analysis of the
2.5 Experimental setup

Figure 2.21: Sketch of the stainless steel manifold fixture for the microreactor. Gas lines machined in the interior of the fixture connect the inlets and outlets of the microreactor to MFCs, a pressure controller (PC), and a QMS.

Figure 2.22: Photograph of the experimental setup.
reaction products and source gas species. To mitigate this problem a continuous flow of argon is introduced in the volume surrounding the O-rings. Thus, any unwanted background due to diffusion through O-rings will be in the form of argon.

The gas flows to the microreactor inlets are controlled by four MFCs allowing mixing of up to four different gases. Outlet 1 on the microreactor (see section 2.2.3) is connected to a pump via a pressure controller. This makes experiments at absolute pressures from 0.1 to 5.0 bar possible. The reactor can be heated from the silicon side using an external resistive heating element covering the outline of the reaction chamber. A large part of the microreactors fabricated in this project contains either integrated resistive temperature detectors (RTDs) or integrated electrodes for electrolysis. In the experimental setup, such components are connected to external electric circuits through wires attached to contact pads on the microreactor chip. The gas flows, the pressure controller, and the heating element are all controlled with a LabVIEW program. When an RTD or electrodes for electrolysis are integrated in the chip, these can also be controlled and monitored with the same LabVIEW program. For microreactors with integrated RTD, the temperature can be controlled using a PID algorithm, allowing temperature changes of up to 1 K s$^{-1}$ and constant temperatures within 0.1 K. The fixture connects outlet 2 on the microreactor to a QMS (Balzers QMA 125) equipped with a secondary electron multiplier. This QMS performs time resolved gas composition analysis.

2.6 Conclusion

The generic design described in this chapter forms the basis of all microreactors developed in the project. Thus, the materials, reaction chamber design, and general channel system topology described in this chapter apply to all the reactors presented in this thesis. Although the various reactors thus share the same basic design, they differ in many respects and are intended for different types of experiments. Much of the terminology introduced in this chapter will be used when each of the reactors are described.
Chapter 3

Microreactor for gas phase reactions

In this chapter, a microreactor intended for gas phase reactions is presented. The device is designed as a highly sensitive analytical tool for measurements of catalytic activity and surface kinetics. Thus, the microreactor can be employed for analyzing the dependence of conversion rate on gas phase stoichiometry and other experimental parameters, like temperature and illumination intensity (in the case of photochemical reactions). In addition, temperature programmed desorption (TPD) can be performed in the chip. Among other things, these kinds of experiments facilitate determination of apparent activation energy and desorption energy for catalytic surfaces. The high sensitivity of the reactor makes it especially well-suited for fundamental catalytic activity studies of model catalysts with low surface areas. A particularly important application is characterization of mass selected metal clusters with a narrow size distribution, as discussed in section 1.1 and 1.4.

Although the high sensitivity is particularly advantageous for fundamental studies involving small quantities of model catalysts, the microreactor is not restricted to these experiments. In addition to deposition from a cluster source, catalyst samples can be introduced into the reactor using a variety of other methods, including flame spray deposition [47], dip-coating, spin coating, or manual deposition with a pipette. During catalyst deposition, a shadow mask can be used to confine deposition to the reaction chamber area. Any catalyst, which can be deposited with these methods and which can fit in the reaction chamber, can be tested with the device. For example, many industrial catalysts with promoters, metal alloys, oxides, and supports can be conveniently tested with the microreactor. The chip is also well-suited for experiments with gas phase photochemical reactions, by virtue of the transparency of the Pyrex lid in the visible and near UV spectrum. Hence, the reactor might be employed for characterization of photocatalysts.

A few reactors for low-area catalyst characterization with gas phase reactions have been reported in literature. Jacobs et al. [48] measured ethylene hydrogenation at atmospheric pressure in a closed tank reactor. They detected catalytic activity on an EBL-nanofabricated platinum model catalyst with a total active surface area of 4 mm². Johansson et al. [12] demonstrated a Pyrex flow microreactor for measuring catalytic activity of nanofabricated model catalysts at atmospheric pressure. In this microreactor, the gas composition was analyzed with a mass spectrometer, which was connected to the reaction zone through a Pyrex capillary, which acted as a flow-limiting orifice. The microreactor had a reaction chamber volume of around 100 mm³, a reaction zone gas flow of about
4 × 10^{16} \text{ molecules s}^{-1}, and a gas residence time in the reaction zone of approximately 60 s. With this setup, oxidation of carbon monoxide was observed on a platinum wire with a surface area of 0.3 mm^2 and on EBL-nanofabricated platinum nanoparticles with a total surface area of 0.4 mm^2. Neither of these two reactor systems were fabricated with batch micromanufacturing techniques. As described in this chapter, significantly higher sensitivity can be obtained with monolithic microdevices.

Numerous silicon-based microreactors for gas phase reactions have been reported in literature. Srinivasan et al. [49] fabricated a silicon microreactor using potassium hydroxide wet etching. The chip was capped from the top with a 1 μm thick silicon nitride membrane and sealed from the bottom with an aluminum plate using epoxy bonding. The chip contained integrated resistive heaters, RTDs, and flow sensors (a hot-wire anemometer), all consisting of platinum thin films. Ammonia oxidation on a platinum thin film catalyst was carried out in the reactor while analyzing the gas composition with a QMS. Srinivasan et al. presented the device as a useful analytical tool for catalyst characterization and also envisioned applications in industrial chemical synthesis by scale-up. Roumanie et al. [50] presented another silicon microreactor fabricated using DRIE and sealed with a Pyrex lid using anodic bonding. As a characteristic feature, the reaction zone in this device included densely distributed silicon pillars in the reaction zone for the purpose of increasing the surface area. The active surface area was further increased either by forming black silicon in the microchannel system or, alternatively, by alumina washcoating. Oxidation of carbon monoxide was carried out on a platinum catalyst to demonstrate the operation of the device. Reaction products were detected with an infrared analyzer. In an ambitious project, Quiram et al. [51–53] fabricated silicon microreactors similar to the ones presented by Srinivasan et al. but bonded with a Pyrex lid using anodic bonding. Several of these reactors were integrated on a modular circuitlike board along with microvalves and micro-MFCs. This board, along with another board containing a feed gas mixing system, fit the slots of a commercial computer chassis, and thus facilitated construction of a compact, automated, integrated microreactor system.

Relatively few papers have been published about photochemical reactions in microreactors, although the number of reported studies has increased significantly in the past two years. Matsushita et al. [54] developed a quartz microreactor for liquid phase photochemical reactions. The device consisted of a single microchannel formed in a quartz substrate using micromilling and sealed with a quartz plate. This reactor was illuminated with lasers and light emitting diodes. The reactor was among other things used to study photocatalytic degradation and reduction of organic compounds dissolved in water and alcohol using titania as a photocatalyst. Gorges et al. [55] fabricated a ceramic microreactor with 19 microchannels formed with milling and sealed with a glass lid using epoxy glue. This device was designed for studies of photocatalytic reactions in liquid phase. Degradation of 4-chlorophenol in aqueous solution on an immobilized titania photocatalyst was used as a model reaction to test the device. In both these reactors the cross sectional dimensions were relatively large being at the order of 100 μm. Very few articles have been published about photocatalytic gas phase reactions in microreactors.

The aim of this chapter is to explain the design and fabrication of the microreactor for gas phase reactions. In addition, testing of the device with respect to reaction zone
3.1 Design

The microreactor consists of a microchannel system which has been etched in a silicon chip with dimensions of $16 \times 20 \text{ mm}^2 \times 350 \text{ μm}$. Fig. 3.1 shows a sketch of the design. The channel system includes two inlets (I1 and I2), through which two different reactant gas mixtures can be introduced and mixed on-chip. The two outlets are referred to as O1 and O2.

The two inlets are connected to a mixing channel of depth 250 μm, which serves two purposes. Firstly, the two reactant gas mixtures entering through I1 and I2 are mixed in the channel. Secondly, the mixing channel acts as a main flow channel with a high gas flow, as described in section 2.2.2 and 2.2.3. To make certain that the two reactant gas mixtures are properly mixed when entering the reaction zone, the mixing channel has a long meander structure and a width of only 150 μm. The mixing channel connects to O1 through a channel with the same depth as the mixing channel. To achieve a high flow conductance this channel has a width of 500 μm. The gas flow through the mixing channel
enters the chip through I1 and I2 and leaves the microreactor through O1. This gas flow is typically on the order of 10 Nml min\(^{-1}\) (4.1 \(\times\) 10\(^{18}\) molecules s\(^{-1}\)).

An inlet channel leads from the mixing channel to the circular reaction chamber with a diameter of 1.0 cm, and an outlet channel leads from the reaction chamber to the flow limiting gas capillary. The inlet channel, reaction chamber, outlet channel, and capillary all have depths of 3 \(\mu\)m. The capillary has a width of 5 \(\mu\)m and a length of 1500 \(\mu\)m. Gas flows from the mixing channel through the inlet channel into the reaction chamber. Subsequently, the gas proceeds through the outlet channel and the capillary to O2. Under typical experimental conditions, this reaction zone gas flow is around 3 \(\times\) 10\(^{14}\) molecules s\(^{-1}\). As described in section 2.4, the purpose of the shallow inlet channel connecting the mixing channel to the reaction chamber is to limit back-diffusion of reaction products to the mixing channel. O2 is connected to the QMS, which analyzes the composition of the gas leaving the reaction chamber. As discussed in section 2.3.2 the reaction chamber contains silicon pillars to prevent a cavity collapse during anodic bonding.

In addition to the reactor design presented above, another similar chip has been fabricated with a wider gas capillary. On this chip, the capillary has the same depth and length, but the capillary width is 54 \(\mu\)m instead of 5 \(\mu\)m. Apart from the capillary dimensions and some minor details concerning the mixing channel geometry, the wide and narrow capillary chips are completely identical. Having access to two different chip designs is an advantage since it allows experiments with different gas flows through the reaction zone. For a given reaction zone pressure, temperature, and gas composition, the gas flow will be about ten times higher for the wide than for the narrow capillary chip. A higher reaction zone gas flow yields a higher space velocity at the expense of lower sensitivity, as seen in Eq. (2.14). Thus, the choice between the two reactor designs depends on the experiment, i.e. whether fast response or high sensitivity are most important in the particular measurement.

### 3.2 Fabrication

The microreactor consists of two parts; a structured silicon chip and a Pyrex lid. The two parts are manufactured separately and are bonded to each other after catalyst deposition. This section describes the fabrication of the silicon chip and the Pyrex lid.

#### 3.2.1 Silicon chip

The microreactor is fabricated using UV lithography, RIE, and DRIE. The fabrication sequence for the silicon chips is illustrated in Fig. 3.2 and is described below.

1. The starting point is a 350 \(\mu\)m thick double side polished 4” (100) silicon wafer. First, what will later become the substrate back is spincoated with a 10.0 \(\mu\)m thick layer of AZ4562 photoresist. A pattern containing the in- and outlet holes is defined in the polymer using UV lithography.

2. Using DRIE, the wafer is etched to a depth of around 100 \(\mu\)m. Subsequently, the polymer mask is removed using acetone.
3. The front side of the substrate is now spincoated with a 1.5 μm thick layer of AZ5214 photoresist. A pattern containing the reaction chamber and the capillary is then defined in the polymer using UV lithography. This pattern also includes the two microchannels leading from the mixing channel to the reaction chamber and from the reaction chamber to the capillary, respectively.

4. The wafer is etched to a depth of 3.0 μm through a RIE process. After etching the low flow part of the channel system, the polymer mask is removed in acetone.

5. The front side of the wafer is covered with a 10.0 μm thick layer of AZ4562 photoresist, and a pattern containing the mixing channel is defined using UV lithography.

6. The back of the wafer is bonded to a handle wafer using photoresist as an adhesive. The handle wafer is required since the in- and outlet holes will subsequently be etched all the way through the wafer. In the DRIE tool helium gas is used to cool the back of the wafer during etching. If no handle wafer were used, the helium gas would leak into the plasma chamber through the inlet and outlet holes.

7. The mixing channel pattern is etched using DRIE until it reaches the in- and outlet holes at a depth of approximately 250 μm. Afterwards, the remaining photoresist and the handle wafer are removed in acetone.

8. As a final fabrication step, the wafer is thermally oxidized (after an RCA cleaning process) with an oxide thickness of 50 nm. Subsequently, the wafer is sawn into small chips, each containing one microreactor.
9. The catalyst material is then deposited on each chip. Different deposition methods have been used.

10. Finally, a Pyrex lid is bonded to the chip using anodic bonding.

Fig. 3.3 shows a photograph of the finished silicon chip bonded to a blank Pyrex lid, without catalyst in the reaction chamber. Fig. 3.4 shows a photograph of the silicon chip without a lid. With the photolithographic masks used in this project, 16 microreactors are produced from a single 4” silicon wafer, with eight wide and eight narrow capillary chips on each wafer.

3.2.2 Pyrex lid

Depending on the application, sealing might be achieved with a blank Pyrex lid or, alternatively, a Pyrex lid with an integrated RTD for temperature measurements. In the latter case, the side of the Pyrex lid facing away from the silicon chip includes an RTD consisting of a structured platinum thin film, as shown in Fig. 3.5. The temperature is determined with a four-point probe measurement of the resistance of a meander path in the center of the lid. The meander path is 80 μm wide. A Pyrex lid with an RTD has dimensions of \(16 \times 32 \text{ mm}^2 \times 500 \mu\text{m}\), whereas blank Pyrex lids have a thickness of 500 μm and the same width and length as the silicon chip. In general, RTD lids are used in experiments with TPD and heterogeneous catalysis where the reactor is heated to elevated tempera-
Figure 3.4: Photograph of a finished narrow capillary silicon chip without lid. With no lid, the shallow part of the channel system is only barely visible with the naked eye. This is in contrast to chips bonded to a Pyrex lid, for which the shallow channels are clearly visible due to interference, as seen in Fig. 3.3.

In photocatalysis experiments, blank lids are in general used to allow illumination of the entire reaction chamber without reflections from a platinum thin film.

In the following, the fabrication of Pyrex lids equipped with RTDs will be described. These lids are fabricated using UV lithography, physical vapor deposition (PVD), and a lift-off process in acetone. The fabrication sequence is illustrated in Fig. 3.6 and described in the following.

1. The starting point is a 500 μm thick 4'' Pyrex wafer. First, what will later become the RTD side of the lid is covered with a 10 nm thick aluminum thin film using electron-beam (e-beam) PVD. The aluminum layer acts to promote adhesion between photoresist and the wafer. In addition, the aluminum layer reflects UV light and thus prevents reflections from the chuck in the exposure tool during the lithography process. This is important since the Pyrex wafer is transparent to UV light.

2. A 1.5 μm thick layer of AZ5214 photoresist is now spun on top of the aluminum, and a pattern containing the RTDs is subsequently defined in the polymer using UV-lithography. As a part of the lithography-process the photoresist is developed in an aqueous sodium hydroxide solution. During this development process, the aluminum below the exposed parts of the photoresist is also etched away.

3. A 10 nm thick titanium thin film is then deposited on the RTD side using e-beam PVD. This titanium layer serves as an adhesion layer between the Pyrex substrate
Figure 3.5: Left: Top view of the Pyrex lid with integrated platinum thin film RTD. In the sketch, the areas covered by platinum are colored black. The temperature is determined with a four-point probe measurement of the resistance of the meander path in the center of the lid. Right: Magnification of the meander path. The meander path is 80 μm wide.

Figure 3.6: Fabrication sequence for Pyrex lid with integrated RTD. See text for descriptions of the individual process steps.
3.2 Fabrication

and the platinum thin film which is deposited next. Subsequently, a 100 nm thick platinum thin film is deposited using e-beam PVD.

4. The polymer mask and the metal on top of it are lifted off in acetone using ultra-sound. This is followed by removal of the remaining aluminum in an aqueous solution of sodium hydroxide. Subsequently, the wafer is sawn out into small chips, each containing one lid. Before the measurements, the RTD is annealed by heating the lid to 400 °C.

After bonding, the position of the RTD matches with the center of the reaction chamber. Fig. 3.7 shows a photograph of the finished Pyrex lid. With the photolithographic masks used in this project, eight identical Pyrex lids with integrated RTDs are produced from a single 4” Pyrex wafer.

At room temperature, the resistance of the meander path is around 470 Ω with a variation of about ±70 Ω between different lids. At other temperatures, the resistance is given by

$$R = R_0 \left[ 1 + \xi_1 (T - T_0) + \xi_2 (T - T_0)^2 \right],$$

(3.1)

where $T_0 = 273.15$ K, $R_0$ is the resistance at $T_0$, $\xi_1 = 0.00381$ K$^{-1}$, and $\xi_2 = -6.02 \times 10^{-7}$ K$^{-2}$. The coefficients $\xi_1$ and $\xi_2$ are parameters characteristic for platinum.

To prepare the microreactor for a catalyst experiment, a catalyst material can be deposited in the reaction chamber using one of the deposition methods mentioned earlier. The microchannel system is subsequently sealed with the Pyrex lid using anodic bonding. This concludes the preparation procedure, and catalyst testing can be initiated. The total preparation time before measurements can be commenced depends on the catalyst deposition method, but is usually around one hour.
3.3 Gas flow

The pressure difference between the reaction chamber and O2 gives rise to a gas flow through the capillary, and the magnitude of the gas flow depends on the exact value of the reaction chamber pressure as well as the temperature. The absolute gas flow through the capillary is an essential design parameter for the following reasons. The reaction chamber and the capillary are connected in series, so the flows through them are the same. Consequently, the residence time of the gas in the reaction chamber can be derived from the capillary flow. Furthermore, knowledge of the gas flow is important for interpretation of experimental results, for instance for determining absolute reaction rates. Finally, when designing the microreactor, the capillary dimensions must be chosen carefully to ensure that the flow to the QMS facilitates optimal gas composition analysis. As mentioned in section 2.1, gas flows through narrow capillaries with vacuum pressure at one end are non-trivial. The reason is that the small cross sectional dimensions might be comparable to the mean free path of the gas, resulting in a noncontinuum flow regime. It follows that it is of interest to measure the capillary gas flow using an absolute method.

The relation between the pressure in the reaction chamber and the gas flow through the capillary was characterized with an experiment, which is described in the following. A narrow capillary microreactor without any catalyst loaded is mounted in the manifold fixture to allow flow from a fixed volume to the QMS. This is done by sealing up the gas lines in the interior of the fixture from the external pump system. Thus, a fixed volume constituted by the microchannel system in the reactor and the gas lines in the interior of the fixture is hermetically sealed. The only path by which gas can leave the volume is by entering the QMS through the on-chip capillary. In this experiment a Baratron (MKS Inc. type 211, 0-1 bar range), which measures the pressure inside the fixed volume, is installed in the fixture. At the onset of the experiment, the fixed volume contains atmospheric air at atmospheric pressure, and the QMS is at vacuum pressure. The fixed volume is 11.2 ml, and the experiment is carried out at room temperature. The pressure is plotted as a function of time in Fig. 3.8(a). As gas flows through the capillary, the pressure in the fixed volume decreases, and the flow is obtained from the ideal gas law

\[
\dot{N}(t) = \frac{V}{k_BT} \frac{dp_v(t)}{dt},
\]

(3.2)

where \(\dot{N}(t)\) is the net number of gas molecules crossing a cross section of the capillary per unit time, \(p_v(t)\) is the pressure in the fixed volume, \(V\) is the volume, and \(t\) is time. In the experiment the microreactor has a capillary depth of 3.0 \(\mu\)m. In Fig. 3.8(b), \(\dot{N}\) is plotted as a function of the pressure in the fixed volume.

In the following, the gas flow through the capillary is described with a theoretical model for comparison with the experimental results. The width of the narrow capillary is very small compared to the widths of the inlet channel leading from the mixing channel to the reaction chamber and the outlet channel leading from the reaction chamber to the capillary. Consequently the flow resistances of the latter two channels as well as that of the reaction chamber can be safely neglected when predicting the flow entering the QMS. Thus, in this discussion only the flow resistance of the capillary is considered.
Figure 3.8: (a) Measured pressure $p_v$ in the fixed volume as a function of time. (b) Experimentally measured flow as a function of the reaction chamber pressure $p_v$ (circles). The solid curve is the theoretically predicted flow as a function of $p_v$. 
Figure 3.9: Sketch of the capillary showing the reaction chamber side (left) and the QMS side (right). The reaction chamber pressure is \( p_1 \), and the QMS pressure is \( p_3 \). The regions with intermediate and molecular flow are indicated. At the position where the pressure is \( p_2 \), the gas flow changes from intermediate to molecular.

The capillary has a rectangular cross section with dimensions 5 \( \mu m \times 3 \mu m \). However, when attempting to predict the relation between the capillary gas flow and the pressure in the reaction chamber, it is convenient to treat the capillary as having a circular cross section. The advantage of this approximation is that for a circular cross section analytic expressions for the flow exist for both the continuum, intermediate, and molecular flow regimes. In this discussion, a circular cross section of diameter \( d = 4.4 \mu m \) and thus of the same area as the actual rectangular cross section will be assumed.

As mentioned in section 2.1.1, the flow regime depends on the Knudsen number \( \lambda/d \), where \( \lambda \) is the mean free path of molecules in the gas. The mean free path is given by Eq. (2.2) and depends on the average molecular diameter, which is 372 pm for atmospheric air [25]. For a capillary diameter of 4.4 \( \mu m \) this means that at room temperature the flow is intermediate at atmospheric pressure, and that the transition from intermediate to molecular flow occurs at a pressure of around \( 1.5 \times 10^3 \) Pa. In Fig. 3.9 the capillary is shown schematically with the two flow regimes. The inlet pressure is \( p_1 \), and at the pressure \( p_2 \) the flow changes from intermediate to molecular. The pressure in the QMS is denoted \( p_3 \).

Using Eq. (2.2), the expressions Eqs. (2.10) and (2.11) can be combined to obtain an analytical expression for the flow that includes both the intermediate and the molecular flow regimes [57]. In addition, an analytical expression for the fraction of the capillary length where the flow is intermediate can be obtained. For atmospheric air at \( T = 295 \) K and at \( p_v > 0.5 \) bar, the flow is intermediate in more than 98% of the length of the capillary, according to this calculation. In Fig. 3.8(b) the theoretically predicted gas flow as a function of the pressure in the fixed volume is plotted with \( T = 295 \) K, \( \eta = 17.8 \times 10^{-6} \) Pa s, and \( m = 4.81 \times 10^{-26} \) kg (the average molecular mass in the air). Both the intermediate and the molecular flow regimes are taken into account when calculating this gas flow. A good agreement with the experimental data is observed. It is emphasized that the expected gas flow plotted in Fig. 3.8(b) is generated from a purely theoretical model, and that the experimental data are not considered when making this prediction. Thus, the theoretical model presented here is not a fit to experimental data but rather a prediction based entirely on the capillary dimensions, the temperature, and the properties of the gas.

Based on these results, the capillary gas flow at typical experimental conditions can be inferred. It appears from Fig. 3.8(b) that at approximately atmospheric pressure in the
reaction chamber the capillary gas flow is around $6 \times 10^{14}$ molecules s$^{-1}$ at room temperature. At the same pressure and a typical reactor temperature of 250°C, the theoretical model predicts a flow of around $3 \times 10^{14}$ molecules s$^{-1}$, corresponding to a gas residence time in the reaction chamber of around 11 s.

During operation, gas is pumped out of the QMS by a turbo pump. In steady state, the amount of gas flowing through the capillary equals the amount pumped by the turbo pump. The pressure $p_{\text{ms}}$ in the QMS is then given by

$$p_{\text{ms}} = \frac{k_B T_{\text{ms}}}{V_p} \dot{N},$$  \hspace{1cm} (3.3)

where $T_{\text{ms}}$ is the temperature of the gas in the QMS, $\dot{N}$ is the number of gas molecules pumped by the turbo pump per unit time, and $V_p$ is the gas volume pumped by the turbo pump per unit time. $V_p$ is referred to as the pumping speed. It is clear from Eq. (3.3) that the gas flow in turn is determined by the capillary dimensions, these dimensions must be chosen to facilitate a suitable QMS pressure. During the experiment, $p_{\text{ms}}$ is continuously measured with an ion gauge and is in the range $2-10 \times 10^{-7}$ mbar. These pressures are well-suited for QMS analysis suggesting that the capillary dimensions are appropriate. Using Eq. (3.3) the effective pumping speed is determined to be approximately 38 l/s. This is reasonable, since the geometric pump aperture is about 9 cm$^2$ giving a maximum theoretical pumping speed of $\sim 10^6$ l/s.

Although the experimental data in Fig. 3.8(b) are in good agreement with the theoretical prediction, pronounced deviations appear at $p_v = 67$ kPa, $p_v = 80$ kPa, and $p_v = 90$ kPa. These deviations derive from the numerical differentiation of the pressure with respect to time in Eq. (3.2). The deviations are caused by distinct periods of time in the originally measured values of $p_v(t)$ characterized by a relatively abrupt increase of about 200 Pa in $p_v$ followed by a corresponding decrease back to the original level 5-8 hours later. These “bumps” in the measured values of $p_v(t)$ are caused by unstable performance of the Baratron. In spite of this effect the quantitative agreement between experimental data and the theoretical prediction clearly suggests that the gas flow can be understood in terms of the theoretical model outlined above.

### 3.4 Applications in heterogeneous catalysis

To demonstrate the operation of the microreactor, CO oxidation is used as a test reaction

$$2\text{CO}(g) + \text{O}_2(g) \rightarrow 2\text{CO}_2(g).$$  \hspace{1cm} (3.4)

In these experiments, the catalyst consists of circular platinum thin films. In particular, the experiments are performed to test the ability to measure catalytic activity of catalysts with low surface areas. Since one of the main purposes of the reactor design is to improve sensitivity to enable studies on low density mass selected clusters, this is essential information on reactor performance. While platinum thin films are not used as CO oxidation catalysts for practical purposes, they are often used as model systems and for test reactions.
in fundamental catalysis studies [13, 50]. Platinum thin films produced using e-beam PVD and a lift-off process in acetone are used in this work because this is a convenient way of preparing catalysts with well controlled surface areas in the range $10 - 10000 \, \mu m^2$. The relation between the area of the catalyst circle and the lowest temperature at which catalytic activity can be detected in the QMS is investigated for the purpose of determining the sensitivity of the microreactor.

In this section, first the fabrication of the catalytic platinum thin film is explained. Subsequently, the reactivity measurements are described, and the experimental data are analyzed.

### 3.4.1 Fabrication of platinum thin film catalyst

Pyrex lids with RTDs are used in these experiments. A circular platinum thin film, integrated directly on the Pyrex lid, acts as a catalyst in the test reaction. The platinum circle is formed on the side of the Pyrex lid opposite to the RTD, and the position of the circle matches with the position of the RTD and with the center of the reaction chamber. As a starting point, the Pyrex lids are prepared exactly as described in section 3.2.2, but after fabricating the RTD and before the wafer is sawn out, the catalyst circle is formed. This is done by processing the back of the wafer in exactly the same way as the front side (the RTD side), while using a different mask when exposing the polymer to UV light. Hence, the catalyst circle consists of a 100 nm thick platinum thin film in addition to a 10 nm thick titanium thin film in between the platinum and the Pyrex substrate. The finished Pyrex lid is shown in Fig. 3.10. A number of different lids with platinum circle areas ranging from 15 $\mu m^2$ to 5000 $\mu m^2$ is fabricated. By performing measurements with different platinum circle areas, it is possible to investigate the relation between the catalyst area and the lowest temperature at which catalytic activity can be detected.

### 3.4.2 Catalytic activity measurements

The Pyrex lids with integrated catalytic platinum circles are used for oxidation of carbon monoxide. A gas mixture consisting of CO and O2 is used, and the platinum circles have different areas ranging from 15 $\mu m^2$ to 5000 $\mu m^2$. The reaction is run at a pressure of 1.00 bar in a surplus of oxygen, with an O2:CO ratio of 20:1 and with a total flow rate of 8.4 Nml min$^{-1}$ through the mixing channel. After mounting in the manifold fixture, the reactor is heated to 400°C in the reaction gas, until any organic contaminants have been burned away, and the gas system has stabilized. The experiments consist of repeatedly ramping the temperature from 80°C to 350°C at a rate of 400 K/h, activating the CO oxidation.

Fig. 3.11 shows the temperature and the CO$_2$ signal in the QMS, both as a function of time, during a single temperature ramp. This experiment is carried out with a catalyst area of 515 $\mu m^2$, and the CO$_2$ content in the QMS is measured using the mass 44 signal. As the temperature is increased, the CO$_2$ signal rises exponentially until a “light off” phenomenon is seen, and full conversion of CO to CO$_2$ takes place. In Fig. 3.11 the background of CO$_2$ from reactions on the filament in the QMS has been subtracted. The
3.4 Applications in heterogeneous catalysis

CO and O\textsubscript{2} signals are measured simultaneously with the CO\textsubscript{2} signals at mass 28 and 32, respectively. Both signals drop as the CO\textsubscript{2} content increases in accordance with the stoichiometry of the reaction.

At low conversion the CO\textsubscript{2} reaction rate \(\dot{N}_{\text{CO}_2}\) (the number of CO\textsubscript{2} molecules produced in the reaction chamber per unit time) is [1]

\[
\dot{N}_{\text{CO}_2} \simeq A r_0(p_{\text{CO}}, p_{\text{O}_2}, p_{\text{CO}_2}) \exp\left(\frac{-E_a}{k_B T}\right),
\]

(3.5)

where \(A\) is the area of the platinum circle, \(E_a\) is the apparent activation energy, and \(p_{\text{CO}}, p_{\text{O}_2},\) and \(p_{\text{CO}_2}\) are the partial pressures in the reaction chamber of CO, O\textsubscript{2}, and CO\textsubscript{2}, respectively. \(r_0(p_{\text{CO}}, p_{\text{O}_2}, p_{\text{CO}_2})\) is a parameter which depends on the partial pressures and the catalyst. The data from Fig. 3.11 are shown as an Arrhenius plot in Fig. 3.12. Here it can be seen that at low temperature and low conversion the rate follows an Arrhenius behavior as expected, with an apparent activation energy \(E_a\) of 0.99 eV. For all the samples the reactivity exhibited Arrhenius behavior with apparent activation energies in the range 0.91 – 1.40 eV with the highest values found for the measurements with smaller catalyst areas. Contreras et al. [58] performed experiments with CO oxidation on a 15 nm thick platinum thin film deposited using PVD on a silicon(100) wafer with native oxide. At temperatures below “light off” these authors measured an apparent activation energy of 1.17 eV, within range of the values found in this work.
Figure 3.11: Experimental data from oxidation of carbon monoxide in the microreactor using a platinum thin film catalyst. The measured temperature (dashed curve, right ordinate axis) and the CO$_2$ signal in the QMS (solid curve, left ordinate axis) are plotted as a function of time. The catalyst area is 515 $\mu$m$^2$, and the CO$_2$ content is measured using the mass 44 signal in the QMS.

$$I(T) = I_0 \exp(-E_a/k_B T)$$

$E_a = 0.99 \pm 0.02$ eV

$I_0 = 0.02$ A

Figure 3.12: Arrhenius plot of the mass 44 (CO$_2$) signal plotted in Fig. 3.11 (circles). The catalyst area for this experiment is 515 $\mu$m$^2$ platinum. A linear fit of the part of the experimental data, where the reaction exhibits Arrhenius behavior, is also shown (solid line). The slope of the fit corresponds to an apparent activation energy of 0.99 eV.
The microreactor and the corresponding experimental arrangement are designed to facilitate high sensitivity characterization of catalytic reactions. The sensitivity of the setup is now evaluated by considering the smallest catalyst area for which catalytic activity can be detected. The criterion for detection of catalytic activity is that the product QMS current $I_p$ must be distinguishable from the background in the QMS. Thus, $I_p$ must be higher than some threshold value $I_t$, which is determined by the QMS background. For the CO oxidation measurements described here, $I_t$ is defined to be 1.0 pA, since this is significantly higher than the background. The product current increases linearly with the reaction rate $N_p$ in the reaction chamber. It follows that the criterion for detection is satisfied when

$$N_p > N_t,$$

where $N_t$ is the reaction rate which causes a product current $I_t$.

From Eqs. (3.5) and (3.6) it follows that for a given area the temperature must exceed a certain threshold temperature $T_t$ before product formation can be detected. $T_t$ is the temperature which causes a reaction rate $N_t$. Only if the temperature is higher than $T_t$, the catalytic activity is high enough to cause a QMS product signal distinguishable from the background. In view of Eqs. (3.5) and (3.6) the threshold temperature can be predicted.

$$
\frac{1}{T_t} = \frac{k_B}{E_a} \left( \ln A - \ln \frac{N_t}{r_0} \right).
$$

(3.7)

Assuming that $N_t/r_0$ may be considered constant, only $A$ and $T_t$ vary in the CO oxidation experiments. Thus, the inverse threshold temperature plotted against the logarithm of the area should yield a straight line with a slope of $k_B/E_a$. Fig. 3.13 shows the experimental data from CO oxidation in the microreactors. The inverse of the lowest temperature at which CO$_2$ formation can be detected is plotted against the platinum circle area (logarithmic scale). In the data evaluation the threshold current $I_t$ is defined to be 1.0 pA, which is significantly above the background (see Fig. 3.12). From the slope of the best linear fit to the data, an apparent activation energy of 1.02 eV is found. This is within range of the values found from the individual Arrhenius plots.

It appears from Fig. 3.13 that even for the smallest catalyst area of 15 $\mu$m$^2$, conversion into CO$_2$ can be detected at a temperature of $\sim$ 300°C. This temperature can easily be reached with the experimental setup. An area of 15 $\mu$m$^2$ is considerably lower than catalyst areas for other high-sensitivity chemical reactors reported in literature [12, 48]. The experimental data thus demonstrate the high sensitivity of the microreactor and the capability to measure reactivity of small amounts of catalyst.

### 3.5 Applications in photocatalysis

The Pyrex lid used to seal the reactor is transparent to electromagnetic radiation in the visible and near-UV spectrum. Fig. 3.14 shows the transmission spectrum of the 500 $\mu$m
3. Microreactor for gas phase reactions

Figure 3.13: The inverse of the lowest temperature at which CO oxidation can be detected plotted as a function of catalyst area. Experimental data from all measured samples are shown (circles). The abscissa axis has logarithmic scale. The linear fit (solid line) yields an apparent activation energy of 1.02 eV.

To demonstrate photocatalysis in the microreactor, CO oxidation is used as a test reaction. In these experiments, a reactor with a capillary width of 54 μm is used to get a fast response time. The photocatalyst is a commercial TiO$_2$ catalyst (Degussa P25), which is deposited by spin coating an aqueous suspension of the catalyst on the Pyrex lid. During deposition, the lid is masked with blue tape (SWT20, Nitto Scandinavia AB), so catalyst is only deposited in the area corresponding to the reaction chamber. The total amount of TiO$_2$ deposited in the reaction chamber is estimated to have an upper limit of 2.6 μg. One advantage of depositing the photocatalyst on the glass lid instead of on the silicon chip is that the catalyst may be characterized by transmission UV-vis spectroscopy before measurements begin. The reactor is mounted in the experimental setup, and the reaction chamber is irradiated through the Pyrex lid with a small 4 W mercury lamp (UVP model UVGL-15). In the experimental data presented here, the lamp is operated in a mode where the irradiation has a continuous spectrum with wavelengths roughly in the range of 300 – 400 nm. The experiment consists of repeatedly turning the light on and off while monitoring the gas composition with the QMS. The nominal feed gas composition is 6:6:2 (He, O$_2$, CO) by volume, the total reaction chamber pressure is fixed at 1 bar, and the experiment takes place at room temperature. In the QMS, the He, CO, O$_2$, and CO$_2$ signals are monitored on mass 4, 28, 32, and 44, respectively. Fig. 3.15 shows the QMS signals as a function of time while the light is turned on and off. When the light is turned on, the CO$_2$ signal rises abruptly, due to photocatalytic CO oxidation. The other QMS signals are almost unaffected due to low turnover (< 1%). When the light is turned off again, the CO$_2$ signal rapidly decreases, returning to the background level.
3.5 Applications in photocatalysis

Figure 3.14: Measured absorbance (crosses, left ordinate axis) and corresponding transmission (solid line, right ordinate axis) of the 500 μm thick Pyrex lid as a function of wavelength. For wavelengths longer than about 330 nm the transmission is essentially constant at 0.92.

Figure 3.15: Photocatalytic CO oxidation over a Degussa P25 TiO₂ photocatalyst. The QMS-currents are plotted as a function of time for mass 4 (He), 28 (CO), 32 (O₂), and 44 (CO₂), with a logarithmic scale on the ordinate axis. In the figure, the mass is referred to as m/Z (m representing the ion mass and Z representing the charge of the ion). The CO₂ signal increases when the lamp is turned on, due to photocatalytic CO oxidation. The other QMS currents are almost unaffected due to low turnover (< 1%).
The photocatalysis measurements have a very high time resolution. In another experiment it was verified that the system reaches 90% of the steady state level in less than 2 s after the light is toggled. This inherent feature of the microreactor platform allows e.g. fast experiments where the illumination wavelength is scanned. Several other photocatalytic gas phase reactions have been successfully studied in the microreactor by researchers at CINF. These reactions include oxidation of methane, methanol, and ethanol, respectively. The high time-resolution is believed to be a major advantage for experimental studies of photocatalysis. Thus, microreactors of the type presented here is expected to play a central role in the photocatalysis activities at CINF in the future.

3.6 Conclusion

The microreactor presented in this chapter is believed to be a useful analytical tool for catalyst characterization, process optimization and fundamental surface physics studies in gas phase reactions. By designing the microreactor in accordance with the guidelines described in chapter 2, a short response time and a very high sensitivity to low catalyst surface areas are achieved. As a part of this PhD project, hundreds of these microreactors have been fabricated. The devices have subsequently been employed by researchers at CINF at DTU as a platform for characterizing a wide variety of different catalysts. Applications of this reactor involving characterization of photocatalysts are described in two manuscripts, which have not yet been published, and which are included in appendix A. The reactor is applied in ongoing experiments aiming at achieving photocatalytic splitting of water vapor over various photocatalysts. In another series of ongoing experiments the goal is to correlate the morphology and catalytic activity of ruthenium nanoparticles in the methanization reaction (the conversion of carbon monoxide and hydrogen into methane and water vapor). In these measurements, mass selected ruthenium nanoparticles are deposited in the reaction chamber with a magnetron sputtering cluster source.
Chapter 4
Anodic bonding with localized cooling

As described in section 2.3 the microreactors developed in this project are sealed using anodic bonding. Relatively high temperatures are required for this sealing method. Normally, a temperature of at least 250 °C is necessary for bonding of silicon to Pyrex, and in many cases a temperature of 300 °C or more is desirable to reduce the bonding time [59]. For some microreactor experiments, the high temperature might be a disadvantage, since a high temperature might change the properties of the catalyst contained within the reaction chamber. For example, the catalyst might sinter or otherwise lose activity. This can be a problem when characterizing catalysts which are intended for low-temperature applications, and which are not supposed to be exposed to high temperatures during their lifetime. Thus, after bonding, the catalyst sample might differ significantly from the actual catalyst of interest. An example of this is gold based catalysts which sinter considerably at high temperatures. This deactivates the gold catalysts since their activity is dependent on a very small gold particle size.

Anodic bonding can be performed at lower temperatures by using alternative glass types which become conductive at lower temperatures. For instance glasses containing lithium- instead of sodium-ions might be employed; however, this only reduces the minimum temperature down to around 160 °C [60, 61]. In addition, differences in the coefficient of thermal expansion between the glass and silicon might be a problem when using glasses different from conventional borosilicate glass. The microreactors fabricated in this project can also be sealed at low temperatures using epoxy bonding, but this method is problematic due to uncleanliness and leakage. Thus, one of the potential problems with epoxy bonding is that the adhesive might contain contaminating compounds such as sulphur which could poison the catalyst. Because of the low catalyst areas involved even minute amounts of such poisons could completely deactivate the catalyst. For instance, consider a situation where 1% of the reaction chamber ceiling area is covered with a catalytic thin film. This corresponds to a total thin film area of approximately 0.01 cm² and a total number of surface sites of around 10¹³. Assume that only the step sites are active and that these step sites make up 4% of the total number of surface sites. Furthermore, assume that the active surface sites are poisoned by sulphur. Then as little as 4 × 10¹¹ sulphur atoms from the epoxy adhesive are enough to completely deactivate the thin film.

There are several advantages of using anodic bonding for sealing the microreactors, as opposed to other bonding methods. Firstly, anodic bonding provides a hermetic bond
which is necessary because of the low reaction zone gas flow. Even a relatively small leak might be comparable to the gas flow through the reaction chamber. Secondly, anodic bonding does not require ultraclean surfaces. Thus, a tight seal can be obtained even when some amounts of dust and particles are present on the surfaces. This is favorable since ultraclean conditions are not always convenient during catalyst deposition. Hence, in many cases it is expedient to load the catalyst in a standard laboratory under ambient conditions.

Recently, a novel bonding setup has been established at CINF. This setup facilitates anodic bonding of microreactors while maintaining a low temperature inside the reaction chamber. The setup provides local cooling of the reaction chamber area while the remaining part of the chip is bonded at high temperature. Such a configuration is useful since the chip is required to bond only outside of the reaction chamber. In this chapter the setup is described along with testing and characterization of the bonding temperature. The method and results presented in this chapter are also described in [32].

### 4.1 Bonding setup

The setup for locally cooled anodic bonding is illustrated in Fig. 4.1, which can be compared with the illustration of a conventional anodic bonding setup in Fig. 2.6. The silicon/Pyrex stack rests on top of an electrically grounded, cylindrical copper pillar, which is cooled with a coolant flow and thus maintained at a low temperature (typically 6–12 °C, but this could well be lower if required). The copper pillar acts as a heat sink and is only in contact with the silicon chip at the position of the reaction chamber. The purpose is to cool the reaction chamber. From the top, an aluminum cathode is brought into contact with the Pyrex lid. A high voltage (typically 1 kV) is applied to the aluminum cathode, which is heated (typically to ~475 °C) for the purpose of raising the glass temperature. As a distinctive feature, a cylindrical hole has been drilled in the cathode at the position of the reaction chamber, so the lid is only in contact with the hot cathode outside of the reaction chamber. During bonding, the copper pillar and the hole in the cathode are in line with each other.

The top cathode is heated using two commercial 150 W incandescent halogen lamps (Osram) with quartz envelopes. The lamps are embedded in holes, which have been drilled in the cathode. As seen in Fig. 4.1, the copper pillar is connected to a larger copper block, which contains internal channels for coolant flow. The copper block is cooled with a commercial circulating cooling bath, using a mixture of water and ethanol as cooling liquid. This cooling liquid is usually kept at a temperature of about 0 °C. Thermal contact between the silicon and the copper pillar may be improved with conventional heat sink compounds or a thin indium foil. Fig. 4.2 shows a photograph of the setup for locally cooled anodic bonding.

The setup illustrated in Fig. 4.1 has three distinctive features which make it differ from a conventional anodic bonding setup. Firstly, the heat is applied from the glass side. This is convenient since only the glass has to be hot and not the silicon. Secondly, the Pyrex lid is only in contact with the cathode in areas where bonding is required and high temperatures can be accepted. Thirdly, the copper pillar acts as a heat sink which cools
Figure 4.1: Cross-sectional view of the setup for locally cooled anodic bonding. The grounded copper pillar is kept cold and acts as a heat sink during bonding, while the cathode is kept at high temperature so that it simultaneously supplies the high voltage and heats the glass. A cylindrical hole is drilled in the cathode above the copper cold finger, so only a minimum of heat is transferred to the part of the chip containing the reaction chamber.
4. Anodic bonding with localized cooling

Figure 4.2: Photograph of the setup for locally cooled anodic bonding. The dull structure in the top of the picture is the aluminum cathode. The copper block is the large structure below the cathode. The tubing for the coolant flow is also visible in the image.

The setup introduced here has proven to be well-suited for performing anodic bonding of the microreactors with a relatively good yield. At typical conditions, bonding is usually complete within 20-25 min. Naturally, the exact temperature inside the reaction chamber is of high importance. Thus, it is of interest to investigate by how much the reaction chamber temperature is reduced compared to the remaining chip. The rest of this chapter is devoted to theoretical and experimental studies of the reaction chamber temperature during bonding.

4.2 Temperature distribution during bonding

4.2.1 Finite element analysis

A finite element analysis (FEA) was carried out to investigate the temperature distribution in the microreactor during bonding. The calculations were performed using the software package COMSOL MULTIPHYSICS 3.5. In these simulations, the real bonding arrangement is approximated by an axially symmetric geometry similar to the actual setup. With this approximation the problem is reduced from a three-dimensional (3D) to a two-dimensional (2D) calculation, significantly reducing the time consumption of the simulation. The geometry used in the FEA is shown in Fig. 4.3. In the bonding setup a thermal contact resistance is expected between the aluminum and Pyrex. This is represented in the simulations by a narrow subdomain along the aluminum-Pyrex interface, giving rise
4.2 Temperature distribution during bonding

Figure 4.3: Geometry and color plot of the calculated steady state temperature distribution from the FEA. The geometry is an axially symmetric approximation of the real cooled-bonding setup. (a) The entire geometry with equal scale on both coordinate axes. The vertical, dashed, grey line signifies the symmetry axis. The silicon and the glass chip are stacked between the aluminum cathode and the copper heat sink. (b) Magnification of the silicon and glass chip. A high temperature gradient is observed in the part of the Pyrex lid outside the reaction chamber. (c) Magnification of the reaction chamber. The temperature in the chamber is seen to be close to room temperature as a result of the cooled-bonding fixture. Note that in (b) and (c) the scaling of the $x$-axis and the $y$-axis is different.

to a thermal contact resistance of $5 \times 10^{-5} \text{ m}^2 \text{ K W}^{-1}$. The reaction chamber is treated as containing atmospheric air.

The temperature distribution satisfies the heat diffusion equation, which, in steady state and in the absence of interior heat sources, is given by

$$\nabla \cdot (k \nabla T) = 0, \quad (4.1)$$

where $k$ is the thermal conductivity, and $T$ is the temperature.

In modeling physical problems with partial differential equations (PDEs), the interactions of the system with the surroundings are represented through boundary conditions. The boundary conditions applied in the FEA are summarized in Fig. 4.4. First, exterior boundaries are described.

A constant temperature of 475 °C is applied to the right boundary of the aluminum cathode. The bottom of the copper block is set to a constant temperature of 12.5 °C. On the symmetry axis, a symmetry boundary condition is applied. Thus, the conductive heat flux perpendicular to the symmetry axis is set to zero. All remaining exterior boundaries
Figure 4.4: Summary of the boundary conditions applied in the FEA. A constant temperature is applied to the top right boundary of the aluminum cathode and to the lower boundary of the copper cooling block (green). On all other exterior boundaries heat is transferred to the surroundings through free convection and thermal radiation (purple). In the reaction chamber radiation between surfaces is accounted for (light blue). Note that the dimensions are not to scale and that the illustration merely serves to summarize the boundary conditions. The entire geometry with correct scaling is illustrated in Fig. 4.3.
adjoin the air surrounding the setup. The boundary condition applied on these boundaries involves convection and thermal radiation to the surroundings and is given by

$$\mathbf{n} \cdot (k \nabla T) = h(T_{\text{amb}} - T) + \varepsilon (G - \sigma T^4), \quad (4.2)$$

where $\mathbf{n}$ is a normal vector pointing outwards from the surface, $h$ is the convection coefficient, $T_{\text{amb}}$ is the ambient temperature, $\varepsilon$ is the total emissivity of the surface, $G$ is the total irradiation, and $\sigma$ is the Stefan-Boltzmann constant.\(^1\)

The boundary conditions for all exterior boundaries have now been explained. Interior boundaries are described in the following. At the interior boundaries adjoining the reaction chamber thermal radiation emitted from the silicon and Pyrex surfaces can pass through the transparent air and irradiate other surfaces in the reaction chamber. Thus, on these interior boundaries, the temperature satisfies the boundary condition

$$\mathbf{n}_s \cdot (k_s \nabla T_s) + \mathbf{n}_a \cdot (k_a \nabla T_a) = \varepsilon (G - \sigma T^4), \quad (4.3)$$

where subscripts $s$ and $a$ refer to the solid and air sides of the boundary, respectively. $\mathbf{n}_s$ and $\mathbf{n}_a$ are normal vectors pointing outwards from the solid and air domain, respectively. On all other interior boundaries the conductive heat flux perpendicular to the boundary is assumed to be continuous. Internal radiation was accounted for on all boundaries exposed to radiation from other parts of the system.

In Eq. (4.2) and Eq. (4.3) it is assumed that the total absorptivity and total emissivity of the surface are equal. This is strictly valid if the temperature of the surface is equal to that of the irradiation source or, alternatively, if the spectral absorptivity and spectral emissivity are independent of wavelength [46]. However, this requirement is not satisfied in the FEA on exterior high-temperature surfaces. Hence, whereas quite accurate estimates for the total emissivity are provided for the different materials in the FEA, the total absorptivity used in the model is less precise. This inaccuracy is not believed to have a significant effect on the temperature distribution, because the heat flux from absorbed irradiation is very small everywhere relative to the conductive heat flux. In addition, it is noted that at exterior high temperature surfaces the heat flux from absorbed irradiation is also very small compared to the total emissive power. In general heat transfer in the system is entirely dominated by conduction from the aluminum cathode to the copper cooling block. Thus, it was verified with FEA that completely neglecting radiation and convection in the model does not alter the temperature by more than a few Kelvin anywhere in the geometry.

Material properties for the FEA are acquired from [62, 63] (for silicon), the COMSOL MULTIPHYSICS 3.5 material library (for air), table values provided from the manufacturer (for the thermal conductivity of Pyrex), and from [46] (all remaining properties). The temperature variation of these material properties were accounted for in all cases, except from the thermal conductivity of Pyrex. The ambient temperature was set to 22 °C, and the convection coefficient was assumed to be 10 W m\(^{-2}\) K\(^{-1}\), which is a realistic value for free convection in air [64].

The boundary value problem consisting of the PDE Eq. (4.1) and the boundary conditions stated above was solved using COMSOL MULTIPHYSICS 3.5. The General Heat

\(^1\)A thorough overview of terminology related to thermal radiation can be found in [46].
Transfer application mode of the COMSOL MULTIPHYSICS Heat Transfer Module was employed. Standard Lagrange elements second order in temperature and first order in radiosity were used in all subdomains. A mapped mesh was employed inside the reaction chamber due to the large width-to-height ratio of this domain. A free mesh with the “extremely fine” predefined mesh size was used in all other subdomains. Using these settings the model consisted of 16361 elements and 35723 degrees of freedom. The stationary nonlinear solver was used to determine the temperature distribution in the setup.

The temperature distribution predicted by the FEA is shown in Fig. 4.3. It appears that the reaction chamber temperature is maintained at a much lower temperature than the part of the Pyrex lid outside the reaction chamber, where a high temperature gradient is observed. Fig. 4.5 shows the temperature in the reaction chamber as a function of radial position according to the FEA. It is seen that the predicted temperature is below 90 °C everywhere and below 50 °C within the central 8 mm diameter circle in the chamber. In the center of the chamber the FEA predicts a temperature of around 40 °C. In the model, the total heat flow through the system is equal to the total heat flow entering the setup through the outer boundary of the aluminum block. According to the model, this heat flow is 96 W. This value is obtained from the 2D FEA by integrating the heat flux across the rightmost boundary of the aluminum block and multiplying by $2\pi a$, where $a$ is the distance from the boundary to the symmetry axis.
4.2 Temperature distribution during bonding

Figure 4.6: Thermocouple measurement of the aluminum cathode temperature (solid curve) and RTD measurement of the reaction chamber temperature (dashed curve). The RTD measures the temperature at the Pyrex surface (inside the reactor) in the central ∼3 mm of the reaction chamber.

4.2.2 Temperature measurements

To measure the reaction chamber temperature during bonding, a direct measurement is performed using a Pyrex lid with integrated RTD. The lid is of the same kind as described in section 3.2.2. When placed on top of the silicon chip in the setup, the lid is turned “upside down” so that the platinum RTD is inside the reaction chamber. Consequently, the RTD measures the reaction chamber temperature. In the experiment, the temperature of the aluminum top cathode is monitored with a K-type thermocouple. Anodic bonding with local cooling of the reaction chamber is carried out by applying a voltage of 1 kV and raising the cathode temperature. The experimental data are plotted in Fig. 4.6. It is seen that the cathode temperature stabilizes at ∼475 °C, while the RTD temperature inside the reactor only reaches ∼45 °C. This measured temperature in the center of the reaction chamber is in good agreement with the theoretical value of 40 °C predicted by the FEA (see Fig. 4.5). With such a low reaction chamber temperature, bonding can in most cases be performed without risk of changing the properties of the catalyst. Thus, the experiment and the FEA demonstrate the utility of the setup.

To further investigate the accuracy of the FEA, another experiment is carried out for the purpose of determining the heat flow through the aluminum block. The temperature $T$ of the aluminum cathode is monitored with the thermocouple during bonding. The aluminum block is maintained at a typical bonding temperature of around 475 °C for an extended period of time. Abruptly, the heating lamps are turned off, and the temperature of the aluminum block is measured as it cools off (see Fig. 4.7). It is assumed that the block is isothermal due to the high thermal conductivity of aluminum. Then the rate $\dot{Q}$ at which heat is lost by the block after heating is turned off is given by
Figure 4.7: Temperature of aluminum cathode as a function of time in experiment where the heating is abruptly switched off (solid curve). The temperature drops off exponentially as heat is transferred from the cathode through the microreactor to the copper heat sink. By considering the slope of the curve at a given temperature the heat flow through the system can be inferred. The slope at 451 °C is indicated in the plot (dashed line).

\[
\dot{Q} = -\rho V c_p \frac{dT}{dt},
\]

where \( \rho \), \( V \), and \( c_p \) are the mass density, volume, and specific heat capacity under constant pressure of the aluminum block, respectively. Thus, the heat loss rate at a given temperature can be inferred from the experimental data by considering the slope of the curve in Fig. 4.7. In the experiment, \( V = 15.5 \text{ cm}^3 \), \( \rho = 2.70 \times 10^3 \text{ kg m}^{-3} \), and \( c_p = 903 \text{ J kg}^{-1} \text{ K}^{-1} \). At \( T = 451 \text{ °C} \), the slope is given by \( dT/dt = -2.1 \text{ K s}^{-1} \) corresponding to a heat loss rate of \( \dot{Q} = 79 \text{ W} \) according to Eq. (4.4). At a given temperature \( \dot{Q} \) is equal to the amount of heat that must be supplied to the aluminum block to maintain it at that temperature in a steady state situation. Thus \( \dot{Q} \) should be equal to the total heat flow through the system predicted by the FEA. As described in section 4.2.1 the FEA predicts a total heat flow of 96 W when the cathode temperature is 475 °C. For a cathode temperature of 451 °C the total heat flow is 91 W, according to the FEA. This theoretical value is in fairly good agreement with the experimental value of 79 W, considering the simplified geometry used in the FEA.

### 4.3 Conclusion

The method for locally cooled anodic bonding presented in this chapter has proved to be useful for sealing microreactors without exposing the catalyst to high temperatures. It
appears from both the FEA and the direct measurements that the setup acts to keep the reaction chamber close to room temperature. The remainder of the glass lid becomes hot enough for bonding to proceed. The results of the FEA are in good agreement with experimental data. A large amount of microreactors fabricated in this project has been bonded with local cooling. Even though this bonding method has the disadvantages of being slightly more cumbersome and having a slightly lower success rate than conventional anodic bonding, the technique is convenient for catalysts which are prone to deactivation at elevated temperatures.
Chapter 5

Microreactor for gas-liquid phase reactions

In this chapter, a microreactor intended for gas-liquid phase reactions is presented. The reactor is based upon the generic design described in chapter 2. Thus, the device has many similarities with the reactor for gas phase reactions presented in chapter 3. The multiphase microreactor described in the following is intended for experiments with electrocatalysis and photocatalysis in liquid phase, and especially in aqueous phase. Reaction products are transferred by diffusion from the liquid phase into a carrier gas. The composition of the carrier gas is subsequently analyzed with a QMS. The main goal is to employ the microreactor for characterization of photoelectrode materials in photoelectrolysis. As an important feature, the multiphase reactor facilitates electrolysis experiments with simultaneous product detection and measurements of electrode current. In electrolysis studies, monitoring of the electrode current alone is often insufficient, since the current does not necessarily originate from the intended reaction. Unwanted reactions, such as side reactions or corrosion of the electrodes, might occur and give rise to a spurious electrode current [59]. Thus, measuring electrode current with direct concurrent detection of reaction products is an attractive feature when characterizing electrodes in electrolysis and photoelectrolysis. Another advantage of the gas-liquid microreactor presented here is that almost all reaction products are detected with a QMS, facilitating quantitative analysis of reaction products.

Numerous microreactors for gas-liquid phase reactions have been reported in literature, and microreactors of this kind can be classified into different categories [65, 66]. There are basically two different approaches for bringing a gas and a liquid phase into contact inside a microreactor. In the first, a continuous phase microreactor, both phases are continuous and the reactor creates an interface between them. In the second, a dispersed phase microreactor, one phase is dispersed into the other, for example gas bubbles dispersed in a continuous liquid phase. The microreactor presented in this chapter can be classified as a mesh microreactor. This is a particular type of continuous phase microreactor where the gas-liquid interface is stabilized with a highly perforated membrane known as the mesh contactor. The role of the contactor is to establish contact between the two phases while preventing dispersion of one phase into the other. The gas and liquid phases
are at opposite sides of the contactor and are only in contact within small openings in the membrane. Phase intermixing is normally avoided by providing a slightly higher pressure in the gas phase than in the liquid phase.

A number of mesh microreactors has been reported in literature. Wenn et al. [67] fabricated a microreactor with a mesh contactor made in nickel using photolithography and a two-stage electroplating method. The membrane was around 5 \( \mu \text{m} \) thick with 5 \( \mu \text{m} \) diameter circular holes. Gavriilidis et al. [68] presented a mesh microreactor employing a commercially available stainless steel micromesh. The mesh contactor was 50 \( \mu \text{m} \) thick and had a 76 \( \mu \text{m} \) average hole size and 23\% perforated area. Experiments revealed that breakthrough of gas into the liquid phase occurred at a pressure difference of about 700 – 800 Pa.

The aim of this chapter is to explain the design and fabrication of the microreactor for gas-liquid phase reactions. The ability to carry out electrolysis in this reactor is demonstrated with an experiment with electrolysis of water.

### 5.1 Design

The microreactor consists of a microchannel system which has been etched in a silicon on insulator (SOI) chip with dimensions of 16 \( \times \) 20 mm\(^2 \) \times 351 \( \mu \)m. Fig. 5.1, 5.2, 5.3, 5.4, and 5.5 show sketches of the design. The basic concept is to form the mesh contactor by etching a honeycomb mesh of narrow holes all the way through the device layer of an SOI wafer. The contactor is subsequently released by partly etching away the buried oxide (BOX) layer in an aqueous solution of hydrofluoric acid (HF). Afterwards, a hydrophobic coating is deposited on the contactor to prevent breakthrough of liquid water into the gas phase through the narrow holes. The hydrophobic coating consists of a molecular layer formed using the precursor molecule 1H,1H,2H,2H-perfluorodecyltrichlorosilane (FDTS) with the chemical formula Cl\(_3\)Si(CH\(_2\))\(_2\)(CF\(_2\))\(_7\)CF\(_3\). This teflon-like molecule is deposited on the entire device layer surface using molecular vapor deposition (MVD). Thus, the whole front side of the chip, including the contactor, is hydrophobic. The sidewalls of all mesh holes and through holes are also hydrophobic. As illustrated in Fig. 5.6 FDTS reacts with silicon oxide on the surface under formation of HCl and forms a highly hydrophobic group. Silicon surfaces treated with FDTS have a water contact angle in atmospheric air of around 110\(^\circ\) at room temperature. During experiments, a thin, stationary film of liquid water is confined at one side of the mesh contactor while a carrier gas streams by the membrane on the other side. Reaction products formed at the water side of the contactor diffuse out of the water phase and into the gas phase through the holes in the contactor.

#### 5.1.1 Reaction chamber

The reaction chamber is circular with a diameter of 1.00 cm. It consists of a liquid chamber (at the chip surface) and a gas flow chamber (below the device layer), separated by a highly perforated mesh contactor (formed in the device layer). The flow chamber has a height of 3 \( \mu \text{m} \) and consists of the empty space left behind when the BOX layer is etched away. The liquid chamber consists of a 3 \( \mu \text{m} \) deep recess in the chip front surface and includes silicon
Figure 5.1: Conceptual illustrations of microreactor cross sections. (1) Top view sketch of the gas-liquid phase reactor chip. The dashed, black curve signifies the cross sections. (2) Cross section excluding oxide supports and lid support pillars in the mesh pattern as well as the injection capillary. (3) Cross section including oxide supports and lid support pillars in the mesh pattern as well as the injection capillary.
Figure 5.2: Top view of the gas-liquid phase reactor chip, showing the two inlets I1 and I2 and the two outlets O1 and O2. The etch depth is indicated by the color. I1 is not connected to the channel system and plays no role in the device. The size of the liquid injection capillary has been exaggerated to make it clearly visible. The 3 μm diameter mesh holes are too small to be seen in this figure. Instead, the presence of the mesh pattern is indicated with a green outline of the areas containing the mesh holes. The liquid chamber, contactor and gas flow chamber are stacked on top of each other in the direction perpendicular to the page. The liquid chamber is at the chip surface, the flow chamber is between the device and handle layer, and the contactor is in between the liquid and flow chamber.
Figure 5.3: Top view illustration of mesh pattern. The etch depth is indicated with the same color code in both the left and right image. Left: Sketch of the gas-liquid phase reactor chip. The presence of the mesh pattern is indicated with a green outline of the areas containing the mesh holes. Right: Magnification of the mesh pattern in the contactor area. The mesh holes are seen as red circles in a hexagonal pattern. Areas where the BOX layer is still intact (i.e. has not been etched away) are indicated by a hatching superimposed on top of the depth-signifying color.
Figure 5.4: Top view illustration of the joining groove area. The etch depth is indicated with the same color code in all images. In the top right and top left images the presence of the mesh pattern is indicated with an outline of the areas containing the mesh holes. Top right: Sketch of the gas-liquid phase reactor chip. Top left: Magnification of the mesh pattern strip connecting the main flow channels to the gas flow chamber below the device layer. Within the strip the mesh hole pattern is extended outside the liquid chamber recess. Bottom: Magnification of the mesh pattern around the joining groove. The 3 μm mesh holes are seen as small circles. Areas where the BOX layer is still intact are indicated by a hatching superimposed on top of the depth-signifying color.
Figure 5.5: Top view illustration of the junction between the liquid chamber and the mesh pattern strip. The etch depth is indicated with the same color code in all images. In the top right and top left images the presence of the mesh pattern is indicated with an outline of the areas containing the mesh holes. Top right: Sketch of the gas-liquid phase reactor chip. Top left: Magnification of the mesh pattern strip. Bottom: Magnification of the mesh pattern at the junction between the liquid chamber and the mesh pattern strip. The 3 μm mesh holes are seen as small circles. Areas where the BOX layer is still intact are indicated by a hatching superimposed on top of the depth-signifying color.
pillars to prevent cavity collapse during anodic bonding, as described in section 2.3.2. The contactor is 12 μm thick and is perforated by a honeycomb mesh of 3 μm diameter circular holes.

Fig. 5.3 shows a sketch of the honeycomb mesh, and the details of the mesh pattern are explained in the following. The distance between the centers of two holes in the mesh is 6 μm. During the contactor release etch, the HF solution makes contact with the BOX layer through the holes in the contactor. The acid gradually etches the oxide isotropically and laterally. The duration of the immersion in the acid must be long enough to fully release the contactor, i.e. all oxide below a unit cell of the mesh pattern must be etched away. The robustness of the contactor is ensured by anchoring the contactor to the handle layer by oxide support structures. These support structures consist of intact parts of the BOX layer, i.e. parts which have not been etched away by the HF solution. Such oxide supports are created by including areas in the mesh pattern where holes are absent (see Fig. 5.3). The duration of the oxide etch is optimized to be long enough to fully release the contactor but short enough to leave the oxide supports intact. In most of the fabricated contactors, a single support structure is obtained by excluding a group of 19 adjacent holes from the mesh. Numerous such oxide supports are distributed across the mesh in a honeycomb lattice reminiscent of the mesh pattern itself. In most of the fabricated contactors the distance between the centers of the support structures is 62 – 83 μm. In addition to the support structures, the holes are also absent at the positions of the silicon pillars supporting the glass lid.
As sketched in Fig. 5.2, the microreactor contains a vertical, circular 100 μm diameter liquid injection capillary, which extends from the back of the chip to the liquid chamber. This capillary is isolated from the gas flow chamber by a 250 μm wide barrier of intact BOX layer surrounding the capillary. The barrier is created by excluding the mesh holes from this area, thus protecting the BOX layer during the oxide etch. Liquid is injected into the liquid chamber by depositing a droplet on the back of the chip at the position of the injection capillary. Subsequently, the gas pressure inside the chip is reduced to slightly below one atmosphere, and the liquid is drawn into the liquid chamber under influence of the pressure difference. Ideally, the liquid should not spread beyond the liquid chamber during injection. Thus, it is hoped that the hydrophobic coating on the contactor combined with the small diameter of the mesh holes will prevent breakthrough of the liquid into the flow chamber during injection. After successful injection of the liquid, the gas pressure inside the chip is immediately raised to above one atmosphere to prevent intermixing of the liquid and gas phase.

5.1.2 Microchannel system

Similar to the gas phase reactor described in chapter 3, the channel system includes two inlets (I1 and I2) and two outlets (O1 and O2). However, as seen in Fig. 5.2, I1 is not connected to the channel system and plays no role in the device. The reason for this is explained in the following. As a consequence of the fabrication sequence, the depth of the main flow channel is equal to the combined thickness of the device layer and the BOX layer, which amounts to 18 μm (this is explained in more detail in section 5.2.1). For comparison, the main flow channel in the gas phase reactor is much deeper with a depth of around 250 μm. Since the flow resistance is approximately proportional to the depth to the third power, the main flow channel in the gas-liquid reactor must be very short to ensure that a gas flow of the order of $10^{18}$ molecules s$^{-1}$ can pass through it without a large pressure drop. Consequently, this design does not allow a main flow channel which is long enough to allow proper mixing of two different gas mixtures. Since on-chip mixing is not a possibility, there is no reason to include two inlets in the chip, so I1 has not been connected to the channel system. I2 is connected to O1 through a system of six 600 μm wide and 18 μm deep main flow channels coupled in parallel. The sole purpose of this main flow channel system is to facilitate a large main gas flow through the chip with a relatively low pressure difference between I2 and O1.

An inlet channel connects the main flow channels to the gas flow chamber, and an outlet channel leads from the gas flow chamber to the flow limiting capillary. The gas capillary is 5 μm wide, 3 μm deep and 1500 μm long. It leads to O2, which is connected to the QMS. The main flow channel and the flow limiting capillary are both located at the device layer surface whereas the gas flow chamber is located between the device and handle layer. These two levels of the channel system must be connected so the carrier gas can flow from the main flow channels to the flow chamber and continue to the QMS. Fig. 5.1, 5.4, and 5.5 illustrate the scheme for joining the surface channel system with the gas flow chamber. The inlet and outlet channels both end in an 18 μm deep rectangular joining groove, where the device layer as well as the underlying BOX layer have been completely
etched away. The joining groove is connected to the flow chamber by extending the mesh hole pattern outside of the liquid chamber recess in an approximately 230 μm wide strip. This strip leads from the joining groove to the circumference of the recess constituting the liquid chamber. During the wet etch, when the oxide is removed below the contactor, the BOX layer will also be etched away below this strip. The empty space left behind will form a tunnel, which connects the joining groove to the flow chamber. This connection scheme is expedient since it allows a fairly large separation distance between the liquid chamber recess and the gas channel system on the chip surface. This large distance makes it likely that the anodic bonding will hermetically seal the liquid chamber from the surface gas channels, which is imperative for confining the liquid film.

As mentioned earlier, on-chip mixing is not possible with this design due to the shallow main flow channels. It is emphasized that this is not considered to be a major limitation. In many experiments, such as photocatalytic water splitting, the gas only serves the purpose of carrying products to the QMS, and the gas species are not reactants in the reaction. For these experiments a single inlet is sufficient. Furthermore, the chip presented here is intended as a proof of concept. In future generations of the microreactor more elaborate fabrication schemes could possibly be used to obtain deeper main flow channels.

In addition to the reactor design presented above, similar chips have been fabricated with slightly different designs. In particular, some of the fabricated chips have gas capillaries with a width of 54 μm instead of 5 μm. This is similar to the wide-capillary gas phase reactor described in section 3.1.

5.2 Fabrication

Similar to the gas phase reactor presented in chapter 3, the microreactor consists of two parts; a structured silicon chip and a Pyrex lid. The two parts are fabricated separately and are bonded to each other after catalyst deposition. This section describes the fabrication of the silicon chip and the Pyrex lid.

5.2.1 Silicon chip

The microreactor is fabricated using UV lithography, RIE, and DRIE. The fabrication sequence for the silicon chips is illustrated in Fig. 5.7 and is described below.

1. The starting point is a double side polished 4” (100) SOI wafer. The handle wafer, BOX layer, and device layer thicknesses are 333 μm, 3 μm, and 15 μm, respectively. First, the wafer is thermally oxidized with an oxide thickness of 1.0 μm.

2. Subsequently, what will later become the substrate back is spincoated with a 10.0 μm thick layer of AZ4562 photoresist. A pattern containing the liquid injection capillary and the in- and outlet holes is defined in the polymer using UV lithography.
Figure 5.7: Fabrication sequence for silicon chip. See text for descriptions of the individual process steps.
3. The wafer is immersed in an aqueous buffered solution of HF with a concentration of 5\%_{\text{mass}}, etching away the exposed parts of the oxide.

4. Using DRIE, the wafer is etched until the BOX layer is reached. During this process step, the BOX layer acts as an etch stop. The photoresist and thermal oxide act as an etch mask. After the DRIE process, the photoresist is removed in an oxygen plasma. Subsequently, the oxide mask is removed in an aqueous buffered solution of HF with a concentration of 5\%_{\text{mass}}.

5. The front side of the substrate is now spincoated with a 1.5 \( \mu \text{m} \) thick layer of AZ5214 photoresist. A pattern containing the liquid chamber recess and the gas capillary is then defined in the polymer using UV lithography. This pattern also includes all the gas channels on the chip surface.

6. The wafer is etched to a depth of 3.0 \( \mu \text{m} \) through a RIE process. Afterwards, the polymer mask is removed in an oxygen plasma.

7. The front side of the wafer is covered with a 2.2 \( \mu \text{m} \) thick layer of AZ5214 photoresist. A pattern containing the deep parts of the gas channels, the joining grooves, the mesh pattern, and the liquid injection capillary is defined using UV lithography.

8. The back of the wafer is bonded to a handle wafer using photoresist as an adhesive. The handle wafer is required since the in- and outlet holes will subsequently be etched all the way through the wafer. In the DRIE tool helium gas is used to cool the back of the wafer during etching. If no handle wafer were used, the helium gas would leak into the plasma chamber through the inlet and outlet holes.

9. The wafer is etched using DRIE until the BOX layer is reached everywhere. The BOX layer acts as an etch stop. Afterwards, the handle wafer is removed in acetone. Subsequently, remaining photoresist residues are removed in an oxygen plasma.

10. The BOX layer is now etched in an aqueous buffered solution of HF with a concentration of 5\%_{\text{mass}} until the contactor is completely released. The released parts of the device layer remain anchored to the handle wafer by virtue of the oxide supports.

11. The wafer is thermally oxidized with an oxide thickness of 50 nm.

12. As a final fabrication step, the wafer is coated with a hydrophobic molecular layer using MVD of FDTS. During the MVD, the back of the wafer is covered with blue tape (SWT20, Nitto Scandinavia AB) to prevent deposition of FDTS on this side of the wafer. The entire front side is coated with FDTS (no masking is used apart from the blue tape), and also the mesh hole sidewalls will be hydrophobic after this step. After the process, the blue tape on the back is removed, and the wafer is sawn into small chips, each containing one microreactor.
5.2 Fabrication

Finally, a Pyrex lid is bonded to the chip using anodic bonding.

With the photolithographic masks used in this project, 16 microreactors are produced from a single 4” SOI wafer. Fig. 5.8 shows a photograph of the finished chip bonded to a blank Pyrex lid.

The fabrication sequence outlined above entails a number of challenges which must be addressed for successful completion of the device. In particular, the duration of the two DRIE processes must be timed quite accurately. In both etches it is crucial that the BOX layer is reached, so the duration of the etch should not be too short. On the other hand, the duration should not be too long, because overetching will cause a sideways etch due to charging of the BOX layer and resulting deflection of ions onto the sidewalls [69, 70]. This effect is often referred to as “notching”. Fig. 5.9 shows an example from the first DRIE etch, where notching occurs because of overetching in the liquid injection capillary. Extensive sideways etching is apparent at the interface between handle wafer and BOX layer. Timing the DRIE etches is especially difficult since the depth-to-width ratios of the liquid injection capillary and the honeycomb mesh holes are so large that the depth can not be measured with a standard stylus profiler. Thus, it is not trivial to determine when the oxide layer has been reached in these structures. Determination of etching time is further complicated by the facts that the etch rate of the DRIE tool depends on the mask
Figure 5.9: Scanning electron micrographs of cleaved wafers illustrating the notching effect at the silicon/oxide interface of an SOI wafer. (Left) Severe notching at silicon/oxide interface. Two trenches are almost connected at the oxide interface due to notching. Image courtesy of S. Jensen [69]. (Right) The liquid injection capillary imaged after the first DRIE process. This wafer was removed from the batch and cleaved for the purpose of verifying that the etch extended all the way to the BOX layer. It is seen that the BOX layer has indeed been reached. In addition, it is seen that the trench has been overetched significantly giving rise to a sideways notching of around 40 μm. Image courtesy of T. Pedersen.

pattern, the etch rate is not perfectly uniform across the wafer, and the etch rate can vary significantly from day to day.

During the first DRIE process, it is verified that the liquid injection hole has reached the BOX layer by processing a batch consisting of multiple wafers. After the DRIE process, a single wafer is removed from the batch and cleaved. By imaging the wafer cross section with scanning electron microscopy (SEM) it can be verified that the capillary extends all the way to the BOX layer (see Fig. 5.9). In the second DRIE etch, the duration has been optimized by etching test structures of the honeycomb mesh pattern with different etching times. Subsequently, the test wafers have been cleaved, and their cross sections have been studied with SEM. From the cross section images the etching depths can be determined and the etch rate can be calculated. During the actual fabrication of the reactors, some overetching is allowed when the honeycomb mesh is formed to ensure that the etch will extend all the way to the BOX layer.

Another important parameter in the fabrication sequence is the duration of the HF release etch. The duration must be optimized to be long enough so that the mesh contactor is fully released. On the other hand the duration must be short enough so that the oxide support structures are still present between the handle wafer and device layer. Because of mass transfer limitation effects, the obtained lateral etch rate is not necessarily equal to the
5.2 Fabrication

etch rate obtained when etching a silicon oxide thin film on the surface of a substrate. The duration of the release etch has been optimized with test structures. It has been found that a duration of around 43 min. is appropriate at room temperature for an aqueous buffered solution of HF with a concentration of \(5\%_{\text{mass}}\).

To visualize cross sections of the gas-liquid phase microreactor, an unbonded silicon chip is cleaved and imaged with SEM. Fig. 5.10 and 5.11 show scanning electron micrographs of cross sections of the reactor. Of note in these micrographs is the extensive amount of notching present in the reaction chamber at the interface between the device layer and flow chamber. This pronounced notching is not surprising, since mesh holes of two different depths, namely 12 (inside the reaction chamber) and 15 \(\mu\text{m}\) (in the mesh pattern strips) must be etched during the final DRIE process. Thus, the mesh holes in the reaction chamber will be somewhat overetched during this process step. The level of notching observed in Fig. 5.10 and 5.11 is not believed to be a serious problem for the operation of the device. On the other hand, very pronounced notching (much more extensive than what is seen in these micrographs) would give rise to a porous structure adjacent to the flow chamber, which could potentially cause problems with poor mass transfer of gas species out of the pores. This could have unfavorable results, such as a long reactor memory in terms of gas composition.

5.2.2 Pyrex lid

In the following, the Pyrex lids used in this project for sealing the gas-liquid phase reactor will be described. The lids fabricated in this project are intended for the sole purpose of testing the device. Hence, the aim is to demonstrate the operation of the microreactor. To this end, Pyrex lids are fabricated with two integrated platinum electrodes for electrolysis of water. In the long term, the goal is to use the reactor for characterizing electrode materials for electrolysis and photoelectrolysis. In such experiments the electrode material of interest would be deposited as a thin film on the Pyrex lid. Thus, it is emphasized that the lids described in this section are dissimilar to the lids which will eventually be employed for the microreactor. Nevertheless, the lids presented here are very useful for performing a proof of concept for the device. Schemes for employing the reactor to characterize electrode materials are discussed at the end of this chapter.

The Pyrex lid used in this project has dimensions of \(16 \times 32 \text{ mm}^2 \times 500 \mu\text{m}\), similar to the lid with integrated RTD described in section 3.2.2. The lid contains two integrated electrodes consisting of structured platinum thin films with a comb-shaped geometry, as shown in Fig. 5.12. These electrodes are located on the side of the lid facing towards the silicon chip. The fabrication sequence is the same as for the Pyrex lid with integrated RTD, except that the annealing step in the end is omitted, and a mask containing the electrode structures is used in the photolithography step. After bonding, the gap between the electrodes match with the center region of the liquid chamber.
Figure 5.10: Scanning electron micrographs of cross sections of the gas-liquid phase microreactor. Top: Area around an oxide support structure inside the reaction chamber. A significant amount of notching is observed at the interface between the flow chamber and the device layer. Bottom: Two neighboring oxide supports in the reaction chamber.
Figure 5.11: Scanning electron micrographs of cross sections of the gas-liquid phase microreactor. Top: Rim of the reaction chamber. Bottom: Liquid injection capillary. A 250 μm wide annular area devoid of mesh holes is seen surrounding the capillary. This area ensures that the capillary and the flow chamber are not connected due to notching and the HF release etch.
5. Microreactor for gas-liquid phase reactions

5.3 Electrolysis of water

To demonstrate the operation of the microreactor, electrolysis of water is used as a test reaction. A microreactor with a capillary width of 54 μm is used in the experiment. The silicon chip is bonded to the Pyrex lid, and the reactor is mounted in the experimental setup. The electrolyte is a 0.1 M aqueous solution of perchloric acid (HClO₄). After injecting the solution into the liquid chamber, the gas pressure is raised to about 1.5 bar to stabilize the liquid-gas interface. Throughout the experiment, the gas pressure is maintained at around 1.5 bar. Pure helium is used as a carrier gas, and the experiment takes place at room temperature. The experiment consists of repeatedly ramping the voltage difference between the electrodes from -2 to 2 V at a rate of 20 mV s⁻¹. The contents of hydrogen and oxygen in the QMS are measured using the mass 2 and mass 32 signals, respectively.

Fig. 5.13 shows the voltage, electrode current, and QMS currents during the experiments, all as a function of time. It is seen that the gas-liquid interface is successfully kept stable for around 27 min after which the experiment is discontinued. As the voltage increases, the electrode current and the H₂ and O₂ signals all rise as expected. The experiment thus corroborates the ability to perform measurements of electrode current with concurrent QMS analysis of reaction products. It appears that the H₂, O₂, and current peaks are somewhat larger at positive than at negative voltages. This could be caused by a difference in effective surface area between the two electrodes. Of note in Fig. 5.13 is the high degree of reproducibility in the measurements during successive voltage ramps, indicating stable performance of the microreactor.

It is of interest to evaluate the stoichiometry of the oxygen and hydrogen formation during the experiment. To this end, the QMS currents at mass 2 and 32 must be converted into the number of oxygen and hydrogen molecules entering the QMS per unit time. This conversion is achieved through calibration of the QMS. The calibration is performed using a reference microreactor, which is a gas phase reactor of the kind described in chapter 3. A pump down experiment of the type described in section 3.3 has been carried out on this reference reactor, and consequently the relation between reaction chamber pressure and capillary gas flow at room temperature is known for this device. In the calibration, one measures the QMS current at a given mass signal arising from the known species gas flow through the reference chip. In this way, the sensitivity of the QMS to a given gas species
Figure 5.13: Experimental data from electrolysis of water in the microreactor using platinum thin film electrodes. (Bottom) The measured voltage (dashed curve, left ordinate axis) and electrode current (solid curve, right ordinate axis) are plotted as a function of time. (Top) The QMS currents for hydrogen and oxygen are plotted as a function of time. The increasing voltage causes electrolytic water splitting, giving rise to an electrode current and production of hydrogen and oxygen.
can be determined. Thus, it is possible to determine the ratio between the QMS current for species $i$ and the number of species $i$ molecules entering the QMS per unit time.

Fig. 5.14 shows the experimental data from Fig. 5.13 for a single voltage cycle. The background in the H$_2$ QMS current has been subtracted. The electrode current and hydrogen and oxygen gas flows are plotted versus voltage. By calibration, the gas flows have been converted into the number of gas molecules entering the QMS per unit time. The electrode current is plotted in units of elementary charges per second. The figure thus highlights the stoichiometry of the water splitting reaction. The relative gas flow magnitudes are in fairly good agreement with the water splitting stoichiometry. It is seen that the electron transfer rate is around 30 – 40% higher than the gas flows.

5.4 Outlook

The experience gained with the gas-liquid phase reactor during the electrolysis experiments is believed to be quite promising. The device has been successfully fabricated, and injection of liquid into the reactor has been demonstrated. In addition, it has been verified that it is possible to stabilize the gas-liquid interface and perform experiments for extended periods of time without any clogging caused by liquid spreading into the gas
channels. During operation, some amount of gas from the ambient atmosphere will diffuse through the liquid in the injection capillary and eventually enter the gas flow chamber. However, the experimental data show that the amount of diffusion is low enough not to deteriorate the gas composition analysis.

Some difficulties have occasionally been encountered with the gas-liquid phase microreactor. At times, clogging of the low-flow part of the gas channel system has been observed. In some cases, such clogging can be removed by raising the gas pressure. If this is ineffective, the clogging can sometimes be removed by heating the device to evaporate the water and subsequently inject a new liquid droplet. However, situations have been encountered where the gas channels were clogged irreversibly. In general clogging is believed to be caused by water which scales the hydrophobic barrier and thus breaks through the mesh holes into the gas flow chamber. Such a breakthrough will disconnect the gas main flow channels from the QMS. Permanent, irreversible clogging could occur when small particles suspended in the water are carried to the gas channels during a water breakthrough. In particular the presence of particles in the flow-limiting gas capillary would block the reactor permanently. The possibility of clogging caused by particles suspended in the water phase is especially relevant for experiments where the goal is to measure the photocatalytic activity of semiconductor nanoparticles for liquid phase water splitting.

In spite of these difficulties the experimental results presented in this chapter are encouraging and indicate that the concept can work in practice. Current activities at CINF aim at carrying out electrolysis experiments similar to the ones presented in this chapter, but with an additional reference electrode on the Pyrex lid. It has also been verified that the reactor can measure the photocatalytic activity of semiconductor nanoparticles dispersed in aqueous phase. However, these experiments were complicated by clogging, most likely caused by nanoparticles being transported by water to the gas capillary.

The microreactor is intended for characterization of photoelectrode materials in experiments similar to the electrolysis experiments. Such characterization of photoelectrodes could be carried out with a modified version of the Pyrex lid, as sketched in Fig. 5.15. The electrode material of interest is deposited as a thin film on top of one of the electrodes. Since it must be possible to irradiate the semiconductor thin film with visible and UV-light, the carrier electrode must be transparent to this spectrum of light. Only a limited range of electric conductors exists which meets this demand. One attractive candidate is indium tin oxide (ITO) which is employed as a transparent, conductive coating in several applications. The platinum electrode in Fig. 5.15 acts as a counter electrode in the photoelectrolysis. This counter electrode remains essentially unchanged compared to the Pyrex lid sketched in Fig. 5.12.

The microreactor design could be optimized based on the experience gained during the preliminary testing. In particular, a wider water injection capillary could ease the injection process and perhaps make it possible to draw liquid into the reactor at a lower pressure difference, reducing the risk of water scaling the contactor barrier. In addition, it might be possible to integrate a microstructured size filter in the gas channel system, reducing the risk of particles clogging the gas channels.
Figure 5.15: Illustration of Pyrex lid for characterization of photoelectrode materials. Top: Top view of lid. The black, dashed circle indicates the outline of the reaction chamber. The dashed line indicates the cross section below. Bottom: Cross section of lid. The photoactive material to be characterized is deposited on top of a transparent ITO carrier electrode. The counter electrode consists of a structured platinum thin film. A silver/silver chloride thin film acts as a reference electrode.
This outlook is now concluded with an outline of the long term goals with the gas-liquid phase microreactor. This long term aim concerns characterization of photoelectrodes for photoelectrolysis. Instead of operating with a system where both working and counter electrodes are integrated in the Pyrex lid, as in Fig. 5.15, it would be very attractive to fabricate a reactor, where the working electrode is situated on the Pyrex lid, and the counter electrode is located on top of the mesh contactor. This idea is illustrated in Fig. 5.16. A metal thin film such as platinum is deposited on top of the mesh contactor, and thus the contactor effectively acts as a counter electrode. The device layer could be electrically connected to the bulk silicon chip, hence easing electrical access to the counter electrode. The photoelectrode material is deposited on top of a carrier electrode consisting of a transparent conducting oxide, such as ITO. This design would be a significant improvement to the existing device, since it substantially reduces the electrolyte resistance between the electrodes, facilitating higher electrode currents and higher reaction rates. However, a number of challenges related to the fabrication has to be overcome before the reactor can be produced. One of the problems is that FDTS does not bind chemically to many metals, such as platinum. Deposition of FDTS on a platinum surface will initially yield a high water contact angle similar to FDTS deposited on silicon. However, if the platinum is heated to around 120 °C the surface will readily return to its hydrophilic state. This behavior could be caused by FDTS being physisorbed on the platinum surface instead of reacting chemically as illustrated in Fig. 5.6. When the temperature is raised, the FDTS desorbs again. It follows that during fabrication of the modified mesh reactor illustrated in Fig. 5.16, the counter electrode thin film must be deposited without covering the side walls of the mesh holes with metal. Otherwise, much of the hydrophobic nature of the contactor might be lost. Such highly directional metal thin film deposition is not trivial. Fabrication of the modified mesh reactor is further complicated by the fact that it is difficult to spin a uniform photoresist layer on a structured surface with large height variations, such as the perforated mesh contactor. Notwithstanding these obstacles, an ingenious process sequence might overcome the challenges and thus permit successful fabrication of the reactor sketched in Fig. 5.16. This device could be very useful for characterization and development of photoelectrode materials.

5.5 Conclusion

The mesh microreactor for gas-liquid phase experiments presented in this chapter is a new concept compared to earlier activities at CINF. This device is believed to be a valuable achievement in the project. The test results are promising and indicate that this type of microreactor could potentially be very useful for development of photocatalysts and electrocatalysts in liquid phase reactions. Breakthrough of liquid through the contactor into the gas phase is likely to be one of the main challenges in future development of the device. In spite of this difficulty, the electrolysis data described in this chapter clearly suggest that a stable gas-liquid interface can be maintained for long enough to carry out detailed and accurate measurements.
Figure 5.16: Cross-sectional illustration of micromesh reactor, where platinum has been deposited on the contactor using titanium as an adhesion layer. Top: Cross section of entire device. Bottom: Magnification of part of the liquid chamber, mesh contactor and gas flow chamber. The platinum acts as a counter electrode in the electrochemical cell. The working electrode is deposited on the lid and consists of a photoactive material on top of a transparent conducting oxide.
Chapter 6

Conclusion

The purpose of this project has been to design and fabricate continuous-flow chemical microreactors for catalyst characterization. The devices are intended as analytical tools in experiments concerning heterogeneous catalysis, photocatalysis and electrocatalysis. The reactors are designed for development of novel catalysts with desirable properties and also for fundamental catalysis studies.

All the microreactors fabricated in this project are based on a generic design, which facilitates high sensitivity to low catalyst areas. The reactors consist of a microchannel system etched in an oxidized silicon chip and sealed with a glass lid using anodic bonding. The generic design relies on a gas flow through the channel system and is intended for reactions at pressures at the order of 1 bar. The gas flow contains the reactants and carries the products to a QMS, which analyzes the composition of the gas. An integrated capillary limits the gas flow through the catalyst bed to around $10^{14} - 10^{15}$ molecules s$^{-1}$ at typical experimental conditions, making it possible to direct the entire reaction zone gas flow to enter a QMS. This prevents unnecessary dilution of the reaction products and causes almost all the products to enter the gas analysis tool, thus ensuring a high sensitivity. The residence time of gas in the reaction zone is usually in the range of 1 – 20 s. The relationship between the reaction zone gas flow and the pressure in the reaction chamber has been investigated with a theoretical model, which predicts the gas flow in the capillary to be in the intermediate flow regime. The theoretical model is in good agreement with experimental results.

The generic design includes a circular reaction chamber with a large floor area, since a large area increases the amount of catalyst which can fit on the reaction chamber floor for a given density. This is favorable for the purpose of obtaining a reasonably high reaction rate when the turnover frequency is low, or when a low catalyst density is required to avoid sintering. The circular shape eases catalyst deposition. Since the reaction chamber volume must be low to ensure a short response time, a large floor area entails a very shallow chamber. For this reason experiments have been carried out to investigate the conditions for cavity collapse during anodic bonding of trenches with large width-to-height ratios. In particular the effect of circular silicon support pillars in the reaction chamber to avoid cavity collapse has been studied. For varying pillar densities, 20 μm diameter pillars have been found to be ineffective in preventing cavity collapse. With a distance of 1 mm between individual pillars, both 100 μm and 200 μm diameter pillars have been found
to greatly increase the achievable width-to-height ratio. In addition, it has been found that 200 μm diameter pillars are significantly more effective than 100 μm diameter pillars for avoidance of cavity collapse. Based on these findings, the microreactors have been equipped with 3 μm deep, 1 cm diameter reaction chambers with 200 μm diameter pillars interspaced by 1 mm.

A microreactor for gas phase reactions has been developed and tested. The primary aim of the device is to allow measurements of catalytic activity and surface kinetics of model catalysts, which can only be obtained in small quantities, thus necessitating high sensitivity to low surface areas. In particular, the reactor is well-suited for characterization of mass selected metal clusters from a magnetron sputtering cluster source. In addition, the microreactor can be employed as a platform for testing of a wide variety of different catalysts, including industrial catalysts. Oxidation of carbon monoxide on low-area platinum thin films has been carried out in the reactor as a test reaction to demonstrate the operation of the device. The experimental data show that for this reaction and under the conditions used in these experiments, catalysts with surface areas as low as 15 μm² can be conveniently characterized with the microreactor. This catalyst area is considerably lower than for other high-sensitivity chemical gas phase reactors reported in literature. In addition, it has been demonstrated that the microreactor is well-suited for experimental studies of photocatalysts. At the time of writing, the gas phase microreactor has been employed by researchers at CINF at DTU as a platform for characterizing a wide range of different catalysts.

At CINF, a setup has been established for performing anodic bonding with local cooling of the reaction chamber. The aim is to avoid deactivation of catalysts in the microreactor caused by the high temperatures associated with anodic bonding. A finite element simulation has been carried out of the temperature distribution in the setup during bonding to investigate the temperature in the reaction chamber. The simulation predicts a temperature in the range of 40 − 50 °C within the central 8 mm diameter circle in the chamber during bonding. This temperature range is in good agreement with experimental results. The setup has proven to be a useful method for performing anodic bonding of the microreactors without deactivation of the catalyst. Thus, locally cooled anodic bonding is now widely used at CINF for bonding microreactors.

A mesh microreactor for experiments involving both a gas and a liquid phase has been developed and tested. The main goal with this device is to allow characterization of photoelectrode materials for photoelectrolysis. The primary advantage of the reactor is that it allows concurrent measurements of electrode current and direct detection of reaction products. The working principle of the reactor is to confine a thin, stationary liquid film on one side of a highly perforated, hydrophobic membrane while a carrier gas streams by the membrane on the other side. This design yields very effective mass transfer from the liquid to the gas phase. Electrolysis of water with platinum thin film electrodes has been carried out in the reactor as a test reaction to demonstrate the operation of the device. Stoichiometric formation of hydrogen and oxygen has been observed in these experiments, and the electron transfer rate was around 30 − 40% higher than the stoichiometric transfer rate. Stable confinement of the liquid water film over a period of 25 min. has been demonstrated during experiments. Thus, the test experiments clearly suggest that a stable
gas-liquid interface can be maintained for long enough to carry out detailed and accurate measurements. The test results are promising and indicate that this type of microreactor could potentially be very useful for development of photocatalysts and electrocatalysts in liquid phase reactions.

In general, the gas phase microreactor is considered to be a rather mature and reliable device at the time of writing whereas the gas-liquid phase reactor is still an emerging technology. A number of improvements to the microreactors can be envisioned as areas for future work. Modification of the two-phase reactor to integrate the counter electrode on the contactor would be a significant improvement to this reactor. In addition, more efficient confinement of the liquid phase would be very convenient. It would be interesting to observe if a wider injection capillary allows liquid injection at a higher flow chamber pressure. If this were the case, it could possibly make it easier to avoid breakthrough of the liquid into the gas phase during injection. Finally, an on-chip valve at the position of the gas capillary would be a very valuable improvement to the microreactors. Such a valve could play the role as a gas capillary with an adjustable flow conductance. It would be possible to effectively turn the microreactors into batch reactors by closing the valve for a period of time followed by release of the gas into the mass spectrometer. Thus, an on-chip valve could bring the sensitivity to low catalyst areas close to a level which would allow measurements on a single catalytic nanoparticle.
Bibliography


Appendix A

Publications

The following list contains contributions to scientific journals presenting research results from the PhD project. At the time of writing, the manuscripts *Highly sensitive silicon microreactor for catalyst testing*, *Anodic bonding with cooling of heat-sensitive areas*, and *Sensitivity study of micro four-point probe measurements on small samples* have been published in peer reviewed journals. The manuscript *Gas-phase photocatalysis in μ-reactors* has been accepted for publication in the peer reviewed *Chemical Engineering Journal* but has not been published yet. The manuscript *Quantitative measurements of photocatalytic CO-oxidation as a function of light intensity and wavelength over TiO$_2$ nanotube thin films in μ-reactors* has been submitted to the peer reviewed *The Journal of Physical Chemistry C*, but has not yet been accepted for publication.


In this appendix, article 1, 2, and 4 are included in their final forms. Article 3 is not included in this appendix since its topic falls outside the field of chemical microreactors,
and because my contribution to this paper has been a modest side activity in my PhD project. Article 5 appears in this appendix in its current form, but it might undergo revision before publication.
Highly sensitive silicon microreactor for catalyst testing

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A novel microfabricated chemical reactor for highly sensitive measurements of catalytic activity and surface kinetics is presented. The reactor is fabricated in a silicon chip and is intended for gas-phase reactions at pressures ranging from 0.1 to 5.0 bar. A high sensitivity is obtained by directing the entire gas flow through the catalyst bed to a mass spectrometer, thus ensuring that nearly all reaction products are present in the analyzed gas flow. Although the device can be employed for testing a wide range of catalysts, the primary aim of the design is to allow characterization of model catalysts which can only be obtained in small quantities. Such measurements are of significant fundamental interest but are challenging because of the low surface areas involved. The relationship between the reaction zone gas flow and the pressure in the reaction zone is investigated experimentally. A corresponding theoretical model is presented, and the gas flow through an on-chip flow-limiting capillary is predicted to be in the intermediate regime. The experimental data for the gas flow are found to be in good agreement with the theoretical model. At typical experimental conditions, the total gas flow through the reaction zone is around \(3 \times 10^14\) molecules s\(^{-1}\), corresponding to a gas residence time in the reaction zone of about 11 s. To demonstrate the operation of the microreactor, CO oxidation on low-area platinum thin film circles is employed as a test reaction. Using temperature ramping, it is found that platinum catalysts with areas as small as 15 \(\mu\)m\(^2\) are conveniently characterized with the device. © 2009 American Institute of Physics.

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I. INTRODUCTION

In heterogeneous catalysis, the discovery, characterization, and optimization of catalysts require extensive experimentation and are critical steps in the development of new chemical processes. Traditionally, macroscale chemical reactors such as the idealized plug flow reactor have been used for catalyst testing.1 As a supplement to these traditional reactors, microfabricated reactors have, in recent years, shown promise as versatile analytical tools for measuring catalytic activity. Microfabricated reactors, also known as microreactors, are chemical reactors with dimensions in the micrometer range. Pioneered by, among others, Jensen et al., microreactors have been shown to offer a number of advantages compared to conventional macroscale reactors.2–6 The temperature of a microreactor can be varied easily and quickly because of the small size. Due to the high surface-to-volume ratio, heat transfer to and from the reaction zone is greatly enhanced. This reduces thermal gradients in the reactor and makes accurate control of temperature possible, even for strongly exothermic reactions. Furthermore, the small dimensions of the reactor improve mass transfer and reduce concentration gradients. Small thermal and concentration gradients are favorable when determining kinetic data. Reaction parameters such as pressure, residence time, and flow rate are more easily controlled in reactions that take place in small volumes. In addition to these advantages, the small scale of the reactor improves safety of use for explosive mixtures and greatly reduces reactant gas consumption. Finally, it is possible to integrate heaters and sensors directly into microreactors using microfabrication technology.

Fundamentally, a microreactor consists of a system of microchannels in which the reactants will flow and react. The flow through the microchannels is mostly laminar, resulting in predictable and well-controlled flow patterns. Due to the small dimensions, the residence time of the reactant gas in the catalyst bed is typically low. Consequently, high space velocities can be obtained.

In combination with an appropriate instrument for gas composition analysis, it is possible to design microreactors which facilitate detection of very small amounts of gas phase products. This is a consequence of the low flow rate through the microchannel system. High sensitivity product detection under atmospheric pressure is useful in several respects. When investigating new, nonoptimized catalysts, the catalytic activity might be low, necessitating detection of very small amounts of gas phase products. Furthermore, some model catalysts, such as mass selected clusters and catalysts fabricated using electron-beam lithography (EBL), can only be obtained in small quantities. Thus, a sensitive experimental arrangement is required for measuring the catalytic activity of such samples.2–9

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A few microreactors for low-area catalyst characterization with gas-phase reactions have been reported in literature. Johansson et al.\textsuperscript{10} demonstrated a Pyrex flow microreactor for measuring catalytic activity of nanofabricated model catalysts at atmospheric pressure. The microreactor had a reaction chamber volume of around 100 mm\(^3\), a reaction zone gas flow of about \(4 \times 10^{10}\) molecules s\(^{-1}\), and a gas residence time in the reaction zone of approximately 60 s. They observed CO oxidation on a platinum wire with a surface area of 0.3 mm\(^2\). Jacobs et al.\textsuperscript{10} measured ethylene hydrogenation at atmospheric pressure in a closed tank reactor. They detected catalytic activity on an EBL-nanofabricated platinum model catalyst with a total active surface area of 4 mm\(^2\).

Our research group has previously fabricated microreactors and applied them in experiments concerning catalysis and surface science.\textsuperscript{11–14} In this paper, we present a novel continuous-flow microreactor with a highly improved sensitivity for measurements of catalytic activity. The device is intended for gas-phase reactions at pressures in the range of 0.1–5.0 bar. The gas composition is analyzed using a quadrupole mass spectrometer (QMS). As a characteristic feature, the microreactor presented here directs the entire reaction zone gas flow to enter the mass spectrometer. This increases the sensitivity considerably compared to traditional microreactors where only a small fraction of the gas flow is analyzed.

The microreactor is designed as an analytical tool for catalyst testing. In this context, the term catalyst testing covers measurements of catalytic activity, turnover frequency, apparent activation energy, and surface area, as a result of temperature programmed desorption and experiments with conversion rate as a function of temperature and gas phase stoichiometry. The high sensitivity of the reactor makes it especially well-suited for fundamental catalytic activity studies of model catalysts with low surface areas. A particularly important application is the characterization of mass selected metal clusters with a narrow size distribution. Such measurements are of significant interest for the purpose of correlating size and catalytic activity of clusters.\textsuperscript{15–17} Often, a low density of clusters is desirable in these studies to suppress sintering effects. Ensembles of metal clusters can be produced with a magnetron sputtering cluster source, but only in small quantities per unit time, since the cluster beam intensity decreases with reduced spread in the cluster size. Thus, a highly sensitive measurement technique, like the one presented here, could substantially reduce the time consumption of such experiments.

Although the high sensitivity is particularly advantageous for fundamental studies involving small quantities of model catalysts, the microreactor is not restricted to such experiments. In addition to deposition from a cluster source, catalyst samples can be introduced into the reactor using a variety of other methods, including flame spray deposition,\textsuperscript{18} dip-coating, spin coating, or manual deposition with a pipette. During catalyst deposition, a shadow mask can be used to confine deposition to the reaction chamber area. Any catalyst, which can be deposited with these methods and which can fit in the reaction chamber, can be tested with the device.

For example, many industrial catalysts with promoters, metal alloys, oxides, and supports can be conveniently tested with the microreactor.

In the work presented here, CO oxidation on circular platinum thin films of different areas is employed as a test reaction. The aim of these experiments is to demonstrate the operation of the reactor and the ability to characterize low-area catalysts. While platinum thin films are not used as CO oxidation catalysts for practical purposes, they are often used as model systems and for test reactions in fundamental catalysis studies.\textsuperscript{19,20} Platinum thin films produced using electron-beam (e-beam) physical vapor deposition (PVD) and a lift-off process in acetone are used in this work because this is a convenient way of preparing catalysts with well controlled surface areas in the range 10–10 000 \(\mu m^2\). The relation between the area of the catalyst circle and the lowest temperature at which catalytic activity can be detected in the QMS is investigated with reference to determining the sensitivity of the microreactor.

II. EXPERIMENTAL

A. Microreactor design

The microreactor directs the entire gas flow through the catalyst bed to a QMS, ensuring that almost all reaction products are present in the analyzed gas flow. Thus, unnecessary dilution of products is avoided, resulting in a high sensitivity. This concept places the following demands on the microreactor design: (1) the flow rate through the catalyst bed must be small, since gas can only be allowed to enter the QMS at a low rate. (2) Because of the low gas flow rate, the reaction zone volume must be small to ensure a relatively short gas residence time.

The microreactor consists of a microchannel system which has been formed in a silicon chip using reactive ion etching (RIE) and deep RIE (DRIE). DRIE is a technique with which deep and narrow structures with vertical sidewalls can be etched in silicon.\textsuperscript{21} The chip has dimensions of 16×20 mm\(^2\)×350 \(\mu m\), as shown in Fig. 1. The channel system includes two inlets (I1 and I2), through which two different reactant gas mixtures can be introduced and mixed on-chip. In addition, two outlets (O1 and O2) are included in

\begin{figure}[h]
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\caption{(Color online) (a) Photograph of reactor showing the two inlets I1 and I2 and the two outlets O1 and O2. The dashed red line signifies the cross section shown in the process flow in Fig. 2. (b) Scanning electron micrograph of the junction between the capillary and the outlet O2. (c) Scanning electron micrograph of the mixing channel.}
\end{figure}
the chip. The inlets and outlets all consist of 600 μm diameter holes which extend from the front side to the back of the chip. The two inlets are connected to a mixing channel of depth 250 μm. To make certain that the two reactant gas mixtures are properly mixed when entering the reaction zone, the mixing channel has a long meander structure and a width of only 150 μm. The mixing channel connects to O1 through a channel with the same depth as the mixing channel. To achieve a high flow conductance, this channel has a width of 500 μm. The gas flow through the mixing channel enters the chip through I1 and I2 and leaves the microreactor through O1. This gas flow is typically on the order of 10 NmL min⁻¹ (4.1×10¹⁸ molecules s⁻¹).

A channel leads from the mixing channel to a circular reaction chamber with a diameter of 1.0 cm, and another channel leads from the reaction chamber to O2. These two channels as well as the reaction chamber all have depths of only 3 μm. In experiments, the catalyst is contained within the reaction chamber, and the chemical reaction occurs here. Gas flows from the mixing channel into the reaction chamber and proceeds to O2. The low depth yields a reaction chamber volume of only 240 nl. The purpose of the shallow channel connecting the mixing channel to the reaction chamber is to limit back-diffusion of reaction products to the mixing channel. O2 is connected to a QMS, which analyzes the composition of the gas leaving the reaction chamber. Thus, the entire gas flow through the reaction chamber, and consequently almost all reaction products, enter this QMS. Only reaction products which might back diffuse from the reaction chamber into the mixing channel can elude the QMS.

The QMS is a vacuum system from which gas can only be pumped at a limited pumping speed. For this reason, the connection between the reaction chamber and O2 includes an on-chip flow-limiting capillary with a low flow conductance. The capillary has a width of 5 μm, a depth of 3 μm, and a length of 1500 μm. To facilitate optimal detection, these dimensions of the capillary have been chosen to obtain a gas flow through the reaction chamber of around 3×10¹⁴ molecules s⁻¹ and a resulting QMS pressure of around 10⁻⁷ mbar under typical experimental conditions.

In the experimental setup, the absolute pressure at O1 can be varied in the range of 0.1–5.0 bar. The absolute pressure at O2 is at vacuum level since this outlet is connected to the QMS. It follows that there is a pressure difference of the order of 1 bar across the system. Since the flow conductance of the capillary is much lower than the conductance of any other part of the channel system, almost the entire pressure drop occurs across the capillary. Consequently, the pressure in the reaction chamber is expected to be very close to the controlled pressure at O1.

The gas flow through the reaction chamber is only around 0.01% of the flow through the mixing channel because the flow resistance of the capillary is much higher than that of the mixing channel. This difference in magnitudes of the gas flows is desirable for the following reasons. Since the gas flow through the reaction chamber constitutes the entire flow entering the QMS, this flow determines the pressure in the QMS. Only when the reaction chamber gas flow has an approximate magnitude of 10¹⁴ molecules s⁻¹ will the QMS pressure be compatible with mass spectrometer operation. Concerning the mixing channel, such a low gas flow would be difficult to control with off-the-shelf mass flow controllers (MFCs) and highly impractical when changing the composition of the gas mixture introduced through the inlets. The volume of the exterior gas supply system connected to I1 and I2 in the experimental setup is much larger than the volume of the microchannel system itself. When changing the composition of the gas entering the chip, one, therefore, has to wait for the old gas to be fully washed away from the exterior tubing by the new gas. Until then, the composition of the gas entering the chip does not resemble the one specified by the user. Thus, a relatively high mixing channel gas flow is required to ensure a short gas residence time in the exterior tubing and a practical time-scale for changes of the gas mixtures. For these reasons, O1 has been included in the chip to generate a bypass gas flow on the order of 10¹⁸ molecules s⁻¹. A gas flow of this magnitude can readily be controlled with off-the-shelf MFCs.

In summary, reactant gases are introduced into the reactor through the two inlets. The reactant gas mixture flows through the mixing channel to O1, where it is vented to the atmosphere. However, around 0.01% of the mixing channel gas flow proceeds to the reaction chamber, where the reactants can react and form products under influence of the catalyst. The resulting gas mixture flows from the reaction chamber through the capillary and enters the QMS, where the gas composition is analyzed.

The large area of the reaction chamber increases the amount of catalyst which can fit at the floor of the reaction chamber for a given density. This is favorable for the purpose of obtaining a reasonably high reaction rate when the turnover frequency is low or when a low catalyst density is required to avoid sintering. The circular shape is an advantage since it makes confinement of the catalyst deposition to the reaction chamber easier than it would be, if for instance a long, narrow meander geometry of the same large area were used. When depositing metal clusters from a magnetron sputtering cluster source, the large, circular shape makes it fairly easy to align a shadow mask. When depositing a catalyst manually with a pipette, the high area and circular shape also ease the process. In addition, with a circular design liquid catalyst suspensions deposited in the reactor form a relatively uniform loading. Finally, the circular shape allows easy use of the “locally cooled anodic bonding” method which has been developed for low-temperature sealing of the microreactor. This bonding method is very useful for catalysts, such as gold clusters, which are likely to sinter at elevated temperatures.

After deposition of catalyst in the catalyst bed, the reactor is sealed with a Pyrex lid, using anodic bonding. During the bonding process, the Pyrex-lid and the floor of the reaction chamber will be attracted toward each other by a strong electrostatic force. Because of the low depth-to-diameter ratio of the reaction chamber, the attractive force might cause the Pyrex-lid to get into intimate contact with the floor of the reaction chamber during the anodic bonding. If this happens, attractive surface forces will quickly cause the entire reaction chamber to collapse, permanently bonding the lid to the re-
The microreactor is fabricated using micromanufacturing batch techniques. With these processes, large numbers of reactors can be produced in a short time and at relatively low cost. The silicon chips are fabricated using ultraviolet (UV) lithography, RIE, and DRIE. These are all standard microfabrication processes. The fabrication sequence for the silicon chips is shown in Fig. 2. The starting point is a 350-μm thick silicon wafer. First, what will later become the substrate front side is covered with a 1.5-μm thick layer of AZ5214 photoresist (a photosensitive, etch resistant polymer). A pattern containing the reaction chamber and the capillary is then defined in the polymer using UV lithography, and the wafer is etched to a depth of 3.0 μm through a RIE process. This pattern also includes the two microchannels leading from the mixing channel to the reaction chamber and from the reaction chamber to the capillary, respectively. After etching the low flow part of the channel system, the polymer mask is removed in acetone. A 9.5-μm thick layer of AZ4562 photoresist is then applied to the back of the wafer, and a pattern containing the in- and outlet holes is defined using UV lithography. Now, the front of the wafer is bonded to a handle wafer using photoresist as an adhesive. This is done to protect this side of the wafer, which might otherwise become damaged along the edge during the subsequent DRIE process. The pattern is then etched using DRIE to a depth of 100 μm, followed by removal of the remaining photoresist and the handle wafer in acetone. The front of the wafer is now covered with a 9.5-μm thick layer of AZ4562 photoresist, and a pattern containing the mixing channel is defined using UV lithography. Again, before the subsequent DRIE process, the side of the wafer not covered by photoresist is bonded to a handle wafer. At this point in the process flow, the handle wafer is required since the in- and outlet holes will now be etched all the way through the wafer. In the DRIE tool helium gas is used to cool the back of the wafer during etching. If no handle wafer were used, the helium gas would leak into the plasma chamber through the in- and outlet holes. The mixing channel pattern is now etched using DRIE until it reaches the in- and outlet holes at a depth of 250 μm. Afterwards, the remaining photoresist and the handle wafer are removed in acetone. As a final fabrication step, the chip is thermally oxidized with an oxide thickness of 50 nm. The wafer is sawn into small chips, each containing one microreactor.

To prepare the microreactor for a catalyst test experiment, a catalyst material can be deposited in the reaction chamber using one of the deposition methods described earlier. The microchannel system is subsequently sealed with a Pyrex lid using anodic bonding. This concludes the preparation procedure, and catalyst testing can be initiated. The total preparation time before measurements can be commenced depends on the catalyst deposition method, but is usually around one hour. In the experimental results presented in this article, the catalyst is incorporated on the Pyrex lid surface as a thin film. Thus, no additional catalyst is deposited in the reaction chamber prior to bonding in these specific experiments.

The side of the Pyrex-lid facing the silicon chip includes a circular platinum thin film, as seen in Fig. 3. This platinum circle acts as a catalyst in the test reaction. A number of...
different lids with platinum circle areas ranging from 15 \( \mu m^2 \) to 5000 \( \mu m^2 \) is fabricated. By performing measurements with different platinum circle areas, it is possible to investigate the relation between the catalyst area and the lowest temperature at which catalytic activity can be detected. The other side of the lid is equipped with an integrated four-point probe resistive temperature detector (RTD) consisting of a structured platinum thin film. The positions of the RTD and the catalyst circle both match with the center of the reaction chamber. The Pyrex lid has dimensions of 16 \( \times \) 32 mm\(^2\) \( \times \) 500 \( \mu m \).

The lid is fabricated using UV lithography, PVD, and lift-off processes in acetone. These are all standard microfabrication processes. The fabrication sequence for the lid is shown in Fig. 4. The starting point is a 500 \( \mu m \) thick Pyrex wafer. First, what will later become the RTD side of the lid is covered with a 10 nm thick aluminum thin film using e-beam PVD. The aluminum layer acts to promote adhesion between photoresist and the wafer. In addition, the aluminum layer reflects UV light and thus prevents reflections from the photoresist and the wafer. Since the O-rings are made from an elastomer, a small amount of gas diffusion from the surrounding air into the system is unavoidable, particularly at elevated temperatures. This gives rise to unwanted background signals of \( O_2 \) and \( N_2 \), complicating analysis of the reaction products and source gas species. To mitigate this problem, a continuous flow of argon is introduced in the volume surrounding the O-rings.

Since the O-rings are made from an elastomer, a small amount of gas diffusion from the surrounding air into the system is unavoidable, particularly at elevated temperatures. This gives rise to unwanted background signals of \( O_2 \) and \( N_2 \), complicating analysis of the reaction products and source gas species. To mitigate this problem, a continuous flow of argon is introduced in the volume surrounding the O-rings. Thus, any unwanted background due to diffusion through O-rings will be in the form of argon.

The reactor is heated from the silicon side using an external resistive heating element covering the outline of the reaction chamber. The temperature is measured with four point measurements of the resistance of the integrated RTD. The gas flow to the two inlets is controlled by four MFCs allowing mixing of up to four different gases. Outlet 1 is connected to a pump via a pressure controller (PC). This makes experiments at absolute pressures from 0.1 to 5.0 bar possible. The gas flows, the PC, and the temperature are all controlled with a LabVIEW program. The temperature is
controlled using a PID algorithm, allowing temperature changes of up to 1 K/s and constant temperatures within 0.1 K. Time resolved gas detection is performed with a QMS (Balzers QMA 125) equipped with a secondary electron multiplier.

III. RESULTS AND DISCUSSION

A. Gas flow

The pressure difference between the reaction chamber and O2 gives rise to a gas flow through the capillary, and the magnitude of the gas flow depends on the exact value of the reaction chamber pressure as well as the temperature. The absolute gas flow through the capillary is an essential design parameter for the following reasons. The reaction chamber and the capillary are connected in series, so the flows through them are the same. Consequently, the residence time of the gas in the reaction chamber can be derived from the capillary flow. Furthermore, knowledge of the gas flow is important for interpretation of experimental results, for instance for determining absolute reaction rates. Finally, when designing the microreactor, the capillary dimensions must be chosen carefully to ensure that the flow to the QMS facilitates optimal gas composition analysis. Gas flows through narrow capillaries with vacuum pressure at one end are non-trivial since the small cross sectional dimensions might be comparable to the mean free path of the gas, resulting in a nonviscous flow regime. It follows that it is of interest to measure the capillary gas flow using an absolute method.

To characterize the relation between the pressure in the reaction chamber and the gas flow through the capillary, a microreactor is mounted in the manifold fixture to allow flow from a fixed volume to the QMS. This is done by sealing up the gas lines in the interior of the fixture from the external pump system. Thus, a fixed volume constituted by the microchannel system in the reactor and the gas lines in the interior of the fixture is hermetically sealed. The only path by which gas can leave the volume is by entering the QMS through the on-chip capillary. In this experiment, a Baratron (MKS Inc. type 211, 0–1 bar range), which measures the pressure inside the fixed volume, is installed in the fixture. At the onset of the experiment, the fixed volume contains atmospheric air at atmospheric pressure, and the QMS is at vacuum pressure. The fixed volume is 11.2 ml, and the experiment is carried out at room temperature. The pressure is plotted as a function of time in Fig. 6(a). As gas flows through the capillary, the pressure in the fixed volume decreases, and the flow is obtained from

$$\dot{N}(t) = \frac{V}{k_B T} \frac{dp_v(t)}{dt},$$

where $\dot{N}(t)$ is the net number of gas molecules crossing a cross section of the capillary per unit time, $p_v(t)$ is the pressure in the fixed volume, $V$ is the volume, $k_B$ is the Boltzmann constant, $T$ is the temperature of the fixed volume, and $t$ is time. In the experiment the microreactor has a capillary depth of 3.0 μm. In Fig. 6(b), $\dot{N}$ is plotted as a function of the pressure in the fixed volume.

The gas flow through the capillary is now described with a theoretical model for comparison with the experimental results. The width of the capillary is very small compared to the widths of the channel leading from the mixing channel to the reaction chamber and the channel leading from the reaction chamber to the capillary. Consequently, the flow resistances of the latter two channels as well as that of the reaction chamber can be safely neglected when predicting the flow entering the QMS. Thus, in this discussion only the flow resistance of the capillary is considered.

Gas flow in a tube of characteristic cross sectional width $d$ can be characterized by the Knudsen number $\lambda/d$, where $\lambda$ is the mean free path of molecules in the gas. If $\lambda/d < 0.0091$, the flow is viscous, if $0.0091 < \lambda/d < 1$, the flow is intermediate, and if $\lambda/d > 1$, the flow is molecular.27,28 The capillary has a rectangular cross section with dimensions $5 \times 3$ μm$^2$. However, when attempting to predict the relation between the capillary gas flow and the pressure in the reaction chamber, it is convenient to treat the capillary as having a circular cross section. The advantage of this approximation is that for a circular cross section analytic expressions for the flow exist for all three flow regimes. In

![FIG. 6. (Color online) (a) Measured pressure $p_v$ in the fixed volume as a function of time. (b) Experimentally measured flow as a function of the reaction chamber pressure $p_v$ (blue circles). The red curve is the theoretically predicted flow as a function of $p_v$.](image-url)
this discussion, a circular cross section of diameter $d=4.4 \ \mu m$ and thus of the same area as the actual rectangular cross section will be assumed.

For air at room temperature, the mean free path is given by

$$\lambda = \frac{6.7 \times 10^{-3}}{p} \text{ Pa m},$$

where $p$ is the pressure. For a capillary diameter of 4.4 $\mu m$, this means that the flow is intermediate at atmospheric pressure, and that the transition from intermediate to molecular flow occurs at a pressure of around $1.5 \times 10^5$ Pa. In Fig. 7, the capillary is shown schematically with the two flow regimes. The inlet pressure is $p_1$, and at the pressure $p_2$ the flow changes from intermediate to molecular. The pressure in the QMS is denoted $p_3$.

In the intermediate flow regime, the gas flow through a tube of length $l$ with circular cross section is

$$N = \frac{c}{k_B T} \left( p_1 - p_2 \right),$$

with

$$c = \frac{\pi p d^4}{128 \eta l} + \frac{1}{3} \sqrt{\frac{\pi d^5}{2 \ell v \eta}} \frac{1 + 1.24 d}{\eta},$$

where $\eta$ is the viscosity of the gas, $p = (p_1 + p_2)/2$, $v = m/(k_B T)$, and $m$ is the mass of a single gas molecule. In the molecular flow regime

$$N = \frac{1}{3} \sqrt{\frac{\pi d^5}{2 \ell v}} \frac{p_2 - p_3}{k_B T}.$$

Using Eq. (2), the expressions Eqs. (3) and (5) can be combined to obtain an analytical expression for the flow that includes both the intermediate and the molecular flow regimes. In addition, an analytical expression for the fraction of the capillary length where the flow is intermediate can be obtained. For atmospheric air at $T=295$ K and at $p < 0.5$ bar, the flow is intermediate in more than 98% of the length of the capillary, according to this calculation. In Fig. 6(b), the theoretically predicted gas flow as a function of the pressure in the fixed volume is plotted with $T=295$ K, $\eta=17.8 \times 10^{-6}$ Pa s, and $m=4.81 \times 10^{-26}$ kg (the average molecular mass in the air). Both the intermediate and the molecular flow regimes are taken into account when calculating this gas flow. A good agreement with the experimental data is observed. It is emphasized that the expected gas flow plotted in Fig. 6(b) is generated from a purely theoretical model, and that the experimental data are not considered when making this prediction. Thus, the theoretical model presented here is not a fit to experimental data but rather a prediction based entirely on the capillary dimensions, the temperature, and the properties of the gas.

Based on these results, the capillary gas flow at typical experimental conditions can be inferred. It appears from Fig. 6(b) that, at approximately atmospheric pressure in the reaction chamber, the capillary gas flow is around $6 \times 10^{14}$ molecules s$^{-1}$ at room temperature. At the same pressure and a typical reactor temperature of 250 °C, the theoretical model predicts a flow of around $3 \times 10^{14}$ molecules s$^{-1}$, corresponding to a gas residence time in the reaction chamber of around 11 s.

During operation, gas is pumped out of the QMS by a turbo pump. In a steady state, the amount of gas flowing through the capillary equals the amount pumped by the turbo pump. The pressure $p_{ms}$ in the QMS is then given by

$$p_{ms} = \frac{k_B T_{ms} N}{S},$$

where $T_{ms}$ is the temperature of the gas in the QMS, $N$ is the number of gas molecules pumped by the turbo pump per unit time, and $S$ is the gas volume pumped by the turbo pump per unit time. $S$ is referred to as the pumping speed. It is clear from Eq. (6) that the gas flow through the capillary determines the pressure in the QMS. Since the gas flow in turn is determined by the capillary dimensions, these dimensions must be chosen to facilitate a suitable QMS pressure. During the experiment, $p_{ms}$ is continuously measured with an ion gauge and is in the range $2-10 \times 10^{-7}$ mbar. These pressures are well-suited for QMS analysis suggesting that the capillary dimensions are appropriate. Using Eq. (6), the effective pumping speed is determined to be approximately 38 l/s. This is reasonable, since the geometric pump aperture is about 9 cm$^2$ giving a maximum theoretical pumping speed of $\sim 106$ l/s.

Although the experimental data in Fig. 6(b) are in good agreement with the theoretical prediction, pronounced deviations appear at $p_2=67$ kPa, $p_2=80$ kPa, and $p_2=90$ kPa. These deviations derive from the numerical differentiation of the pressure with respect to time in Eq. (1). The deviations are caused by distinct periods of time in the originally measured values of $p_2(t)$ characterized by a relatively abrupt increase of about 200 Pa in $p_2$, followed by a corresponding decrease back to the original level 5–8 h later. These “bumps” in the measured values of $p_2(t)$ are caused by unstable performance of the Baratron. In spite of this effect, the quantitative agreement between experimental data and the theoretical prediction clearly suggests that the gas flow can be understood in terms of the theoretical model outlined above.

It is noted that other desired values of the capillary flow resistance can easily be obtained by fabricating microreactors with other capillary dimensions. This could be favorable for some experiments. For a constant inlet pressure, an in-
crease of the capillary width would for example result in a shorter reaction chamber residence time.

B. Oxidation of carbon monoxide

To demonstrate the operation of the microreactor, CO oxidation on platinum thin film circles is used as a test reaction. In particular, the experiments are performed to test the ability to measure catalytic activity of catalysts with low surface areas. Since the main purpose of the reactor design is to improve sensitivity to enable studies on low density mass selected clusters, this is essential information on reactor performance. A gas mixture consisting of CO and O2 is used, and the platinum circles have different areas ranging from 15 to 5000 \( \mu \text{m}^2 \). The reaction is run at a pressure of 1.00 bar in a surplus of oxygen, with an O2:CO ratio of 20:1 and with a total flow rate of 8.4 Nml min\(^{-1}\) through the mixing channel. After mounting in the manifold fixture, the reactor is heated to 400 °C in the reaction gas, until any organic contaminants have been burned away, and the gas system has stabilized. The experiments consist of repeatedly ramping the temperature from 80 to 350 °C at a rate of 400 K/h, activating the QMS.

The microreactor and the corresponding experimental arrangement are designed to facilitate high sensitivity characterization of catalytic reactions. The sensitivity of the setup is now evaluated by considering the smallest catalyst area for which catalytic activity can be detected. The criterion for detection of catalytic activity is that the product QMS current exhibits Arrhenius behavior, is also shown (red line). The slope of the fit corresponds to an apparent activation energy of 0.99 eV.

At low conversion, the CO2 reaction rate \( \dot{N}_{\text{CO}_2} \) (the number of CO2 molecules produced in the reaction chamber per unit time) is

\[
\dot{N}_{\text{CO}_2} = A r_0 p_{\text{CO}} p_{\text{O}_2} p_{\text{CO}_2} \exp(-E_a/k_b T),
\]

where \( A \) is the area of the platinum circle, \( E_a \) is the apparent activation energy, and \( p_{\text{CO}}, p_{\text{O}_2}, \) and \( p_{\text{CO}_2} \) are the partial pressures in the reaction chamber of CO, O2, and CO2, respectively. \( r_0 \) is a parameter which depends on the partial pressures and the catalyst. The data from Fig. 8 are shown as an Arrhenius plot in Fig. 9. Here, it can be seen that at low temperature and low conversion the rate follows an Arrhenius behavior as expected, with an apparent activation energy \( E_a \) of 0.99 eV. For all the samples, the reactivity exhibited Arrhenius behavior with apparent activation energies in the range 0.91–1.40 eV with the highest values found for the measurements with smaller catalyst areas. Contreras \textit{et al.} performed experiments with CO oxidation on a 15 nm thick platinum thin film deposited using PVD on a silicon(100) wafer with native oxide. At temperatures below “light off,” these authors measured an apparent activation energy of 1.17 eV, within range of the values found in this work.

FIG. 8. (Color online) Experimental data from oxidation of carbon monoxide in the microreactor using a platinum thin film catalyst. The measured temperature (red, dashed curve, right ordinate axis) and the CO2 signal in the QMS (black, solid curve, left ordinate axis) are plotted as a function of time. The catalyst area is 515 \( \mu \text{m}^2 \), and the CO2 content is measured using the mass 44 signal in the QMS.

FIG. 9. (Color online) Arrhenius plot of the mass 44 (CO2) signal plotted in Fig. 8 (black circles). The catalyst area for this experiment is 515 \( \mu \text{m}^2 \) platinum. A linear fit of the part of the experimental data, where the reaction exhibits Arrhenius behavior, is also shown (red line). The slope of the fit corresponds to an apparent activation energy of 0.99 eV.
since this is significantly higher than the background. The product current increases linearly with the reaction rate \( N_p \) in the reaction chamber. It follows that the criterion for detection is satisfied when

\[
N_p > N_t,
\]

where \( N_t \) is the reaction rate which causes a product current \( I_r \).

From Eqs. (8) and (9), it follows that for a given area the temperature must exceed a certain threshold temperature \( T_t \) before product formation can be detected. \( T_t \) is the temperature which causes a reaction rate \( N_t \). Only if the temperature is higher than \( T_t \) will the catalytic activity be high enough to cause a QMS product signal distinguishable from the background. In view of Eqs. (8) and (9), the threshold temperature can be predicted.

\[
N_t = A r_0 \exp \left( \frac{-E_a}{k_B T_t} \right) \Rightarrow \frac{1}{T_t} = \frac{k_B}{E_a} \left( \ln A - \ln \frac{N_t}{r_0} \right). \tag{10}
\]

Assuming that \( N_t/r_0 \) may be considered constant, only \( A \) and \( T_t \) vary in the CO oxidation experiments. Thus, the inverse threshold temperature plotted against the logarithm of the area should yield a straight line with a slope of \( k_B/E_a \). Figure 10 shows the experimental data from CO oxidation in the microreactors. The inverse of the lowest temperature at which CO formation can be detected is plotted against the platinum circle area (logarithmic scale). In the data evaluation, the threshold current \( I_t \) is defined to be 1.0 pA, which is significantly above the background (see Fig. 9). From the slope of the best linear fit to the data, an apparent activation energy of 1.02 eV is found. This is within range of the values found from the individual Arrhenius plots.

It appears from Fig. 10 that even for the smallest catalyst area of 15 \( \mu m^2 \), conversion into CO2 can be detected at a temperature of \( \sim 300 \) °C. This temperature can easily be reached with the experimental setup. An area of 15 \( \mu m^2 \) is considerably lower than catalyst areas for other high-sensitivity chemical reactors reported in literature. The experimental data thus demonstrate the high sensitivity of the microreactor and the capability to measure reactivity of small amounts of catalyst.

IV. CONCLUSIONS

The microfabricated chemical reactor presented here facilitates highly sensitive catalyst testing. An integrated capillary limits the gas flow through the catalyst bed to around \( 3 \times 10^{14} \) molecules s\(^{-1} \) at typical experimental conditions, making it possible to direct the entire reaction zone gas flow to enter a QMS. This prevents unnecessary dilution of the reaction products and causes almost all the products to enter the gas analysis tool, thus ensuring a high sensitivity. The microreactor can be employed as a platform for testing of a wide variety of different catalysts, including industrial catalysts. However, the primary aim of the device is to allow measurements of catalytic activity and surface kinetics of model catalysts, which can only be obtained in small quantities, thus necessitating high sensitivity to low surface areas. In particular, the reactor is well-suited for characterization of mass selected metal clusters from a sputtering cluster source.

The relationship between the reaction zone gas flow and the pressure in the reaction chamber has been investigated with a theoretical model, which predicts the gas flow in the capillary to be in the intermediate flow regime. The theoretical model is in good agreement with experimental results. CO oxidation on low-area platinum thin films was carried out in the reactor as a test reaction to demonstrate the operation of the device. The experimental data show that for this reaction and under the conditions used in these experiments, catalysts with surface areas as low as 15 \( \mu m^2 \) can be conveniently characterized with the microreactor. This catalyst area is considerably lower than for other high-sensitivity chemical reactors reported in literature.

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Note: Anodic bonding with cooling of heat-sensitive areas

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Anodic bonding of silicon to glass always involves heating the glass and device to high temperatures so that cations become mobile in the electric field. We present a simple way of bonding thin silicon samples to borosilicate glass by means of heating from the glass side while locally cooling heat-sensitive areas from the silicon side. Despite the high thermal conductivity of silicon, this method allows a strong anodic bond to form just millimeters away from areas essentially at room temperature. © 2010 American Institute of Physics. [doi:10.1063/1.3277117]

The highly useful phenomenon—that silicon (with a thin oxide layer) may form an impressively strong bond to glass when the two materials are brought into intimate contact under the influence of strong electric fields and high temperature, anodic bonding (also known as “Mallory bonding,” named after the company where it was invented and patented)—has been known and used for many years.2

The process is particularly useful for microelectromechanical system (MEMS) pressure sensors and other transducers and in weather sealing of solar cells because the bond hermetically seals the surfaces together.3 In our research group we use the process for sealing μ-reactors for catalyst characterization;4 however for this application the high temperatures needed for successful anodic bonding may cause catalysts to sinter or otherwise lose activity. An example of this is Au-based catalysts, which are notorious for deactivating since activity is dependant on very small Au particle size. This paper describes a practical way to overcome this issue by locally cooling the chip while the rest of it bonds. This method has proven practical and reliable in our implementation and could be useful for many other MEMS applications.

In brief, anodic bonding works by applying a large (~kV) negative bias on the glass with respect to the silicon while at the same time heating the stack such that cations in the glass become somewhat mobile. The electric field set up over the interface causes migration of ions (typically Na+ for normal glass types) away from the interface, which sets up an intrinsic electrostatic attraction between the silicon and the glass. No external force is therefore required as the internal forces set up by this field are very strong (pressure in the GPa range).5,5 True chemical bonds are formed between the Si and the glass permanently bonding the two surfaces. A schematic of the process is shown in Fig. 1. The downside of the technique is the inherent necessity of elevated temperatures to give the cations reasonable mobility in the glass.6

In some applications a typical bonding procedure for borosilicate-type glass (e.g., Pyrex) to silicon (e.g., 30 min at 350°C) may well exceed the thermal budget of parts of the device. In such cases the traditional remedy is to use glass types that conduct at lower temperatures. A typical strategy might be a lithium doped glass-ceramics,7 but generally the process still does not work below perhaps 160°C.7,8 and differences in thermal expansion coefficients might be problematic for these glass types, while conventional borosilicate glass is well matched to Si. Another method is low-temperature soldering with, e.g., In/Sn eutectic mixtures,8 however necessary measures to avoid oxidation of the solder make this method unsuited for general use in open air, and the minimum temperature for this method is also ~160°C. Devices may also be sealed with adhesives, but (un)cleanliness and leakage makes this unattractive.

Conventional (hot) anodic bonding is shown in Fig. 1, while the locally cooled-bonding method we have developed may be seen in cross section in Fig. 2. There are a few key differences to note. First, since it is the glass (not the silicon) that needs to be warm we apply heat from the glass side. The heater also serves as high tension cathode. Second, the heater only touches the glass where bonding is needed and heat is acceptable. Third, we have introduced a heat sink (cold finger), which also serves as electrical connection to ground, and the heat sink only touches the silicon in the areas where low temperature (and not bonding) is needed. In our setup, the cold finger supporting the silicon and the hole in the heater are both cylindrical, giving the advantage of radial symmetry (no corners with stress concentration) when parts of the system heat and cool.

As a practical method for heating the top electrode, we use two commercial 150 W incandescent lamps with quartz envelopes (Osram) embedded in holes in the top electrode, which is made of aluminum for its high thermal conductivity. Quartz is insulating well above the relevant temperatures, so the power supply for the filaments does not need galvanic isolation and is indeed grounded in our setup. The heat sink is machined from copper and has internal channels for coolant flow. It is kept at a constant temperature (typically 6–12°C, but this could well be lower if needed) using a commercial circulating cooling bath. Thermal contact between the silicon and the Cu pillar may be assured with conventional heat sink compounds or a thin indium foil. For our conditions (1 kV potential drop and 475°C cathode temperature), bonding is normally complete within 20–25 min.

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In order to find out what the temperature inside the reactor is during bonding, we have performed a direct measurement inside the reactor using resistive temperature detection (RTD) and also carried out a finite-element-type calculation using the COMSOL MULTIPHYSICS 3.5 software package. For the four-point RTD measurement, we have used our standard RTD $\mu$-reactor lids, which incorporate a 100 nm thick platinum four terminal resistor structure and contact pads for making the four connections, as may be seen in Fig. 1 and detailed in Ref. 4. For the purpose of measuring the temperature inside the $\mu$-reactor during bonding, we turned the lid “upside down” so that the Pt RTD was inside the $\mu$-reactor. As a result, the measured RTD temperature corresponds to the temperature inside the reactor. The temperature of the aluminum top cathode was also recorded using a K-type thermocouple. The measurements are plotted in Fig. 3. It is seen that the cathode stabilizes at $\sim475^\circ$C, while the RTD temperature inside the reactor only reaches $45^\circ$C.

In the finite element analysis (FEA), the real bonding arrangement was approximated with an axially symmetric geometry similar to the actual setup. The steady state temperature distribution was computed. The geometry of the FEA and the predicted temperature distribution are shown in Fig. 4. In the bonding setup a thermal contact resistance is expected between the aluminum and Pyrex. This was represented in the simulations by a narrow subdomain along the aluminum-Pyrex interface, giving rise to a thermal contact resistance of $5 \times 10^{-5}$ $\text{m}^2\text{KW}^{-1}$. In the FEA a constant temperature distribution from the FEA. The geometry is an axially symmetric approximation of the real cooled-bonding setup. (a) The entire geometry with equal scale on both coordinate axes. The vertical dashed gray line signifies the symmetry axis. The silicon and the glass chip are stacked between the aluminum cathode and the copper heat sink. (b) Magnification of the silicon and glass chip. A high temperature gradient is observed in the part of the Pyrex lid outside the reaction chamber. (c) Magnification of the reaction chamber. The temperature in the chamber is seen to be close to room temperature as a result of the cooled-bonding fixture. Note that in (b) and (c) the scaling of the $x$-axis and the $y$-axis is different.
temperature of 475 °C was applied to the right boundary of the aluminum block. The bottom of the copper block was set to a constant temperature of 12.5 °C, and the reaction chamber was treated as containing atmospheric air. The FEA gives detailed information about the thermal gradients from which, e.g., heat fluxes and thermal expansion can be extracted. Figure 5 shows the temperature in the reactor chamber as a function of radial position according to the FEA. It is seen that the predicted temperature is below 90 °C everywhere and below 50 °C within the central 8 mm diameter circle in the chamber. In the center of the chamber the FEA predicts a temperature of around 40 °C, which is in good agreement with the experimental result 45 °C (Fig. 3).

For evaluation of the scalability of the method, it is useful to consider a design where the radial distance between heater and cold finger edges is sufficient to ensure that a region (outside the cooled air-gap region) of purely radial heat flow exists. In the present system such a region would be the cylindrical cross section with a radius of ~5.2 mm (to good approximation). In that region the ratio of heat flows in glass $P_{Gl}$ and silicon $P_{Si}$ is $P_{Gl}/P_{Si} = (\kappa_G h_G)/(\kappa_S h_S)$, while the total heat flow is $P_{tot} = P_{Gl} + P_{Si}$, here and below $\kappa$ and $h$ are the thermal conductivities and material thicknesses, respectively. Then, by continuity, in the reactor region the heat flow in the glass will be directed through the air film in the reactor and cause a (mean) temperature difference $\Delta T = P_{Gl}/h_{air}(\kappa_{air} \pi r^2)$ between top and bottom of the reactor; $a$ is the radius of the reactor chamber. It follows that $\Delta T$ will increase approximately linearly with reactor height; in the present design $\Delta T = 4$ K at $h_{air} = 3$ µm, and if arbitrarily the upper acceptable limit is $\Delta T_{max} = 60$ K, then the upper limit on the reactor chamber height is $h_{air} \leq 45$ µm, with all other parameters unchanged. The limit on reactor chamber height may be lifted if forced convection cooling is applied to the glass lid surface through the center bore of the heater.

An increase in the thickness of the glass wafer is also seen to cause an increase in $\Delta T$, but at the same time the heater temperature must be increased since $P_{Si}$ must be maintained to keep the temperature $T_B$ at the bonding interface fixed.

In the heater and cold finger regions, the heat flow is three-dimensional. The transition to a radial heat flow in the heater region takes place on a length scale that is approximately $h_G + 2h_S$, while at the cold finger the transition takes place on a length scale of approximately $h_S$ since here, the main heat flow is in silicon. It follows that the radial distance between heater and cold finger edges must fulfill $\Delta H_{max} = h_G + 2h_S$. Moreover, in the region directly above the cold finger, the length scale of the temperature variation is $h_S$, and thus the cold finger radius must fulfill $r_{cf} > h_S$, say, $2h_S$. A minimum applicable chip size could then be estimated from $2r_{min} = 2(2h_S + h_G + 2h_S + w_H)$, where $w_H$ is the width of the glass-heater contact; this probably has to fulfill $w_H > h_G + h_S$, making $r_{min} > 2(3h_S + 2h_G) = 5.5$ mm with a cold finger radius $r_{cf} = 0.7$ mm. This design was verified by FEA.

With the current design, the temperature $T_{Re}$ in the center of the reactor (on the silicon side) is almost entirely controlled by the Cu cold finger $T_{cf} = T_{cf} + R_{Cu} P_{air}$, where $T_{cf}$ is the cold finger temperature (we have used $T_{cf} = 12$ °C) and $R_{Cu} = \frac{L_{Cu}}{\pi \kappa_{Cu} \rho_{Cu} c_p} + 1/(4\kappa_{Cu} \rho_{Cu})$ is the thermal resistance of the cold finger of length $L_{Cu}$ including thermal spreading resistance to the Cu bulk. It follows that the reactor temperature is linearly dependent on the cold finger temperature, linearly dependent on the total heat flow, and strongly dependent on the cold finger geometry. This also emphasizes the importance of ensuring good thermal contact between silicon and the cold finger; thus we use thermogrease at that junction.

By heating from the glass side of the glass-silicon stack and providing efficient local cooling, we have shown that silicon may be anodically bonded to glass successfully while keeping small (<1 cm) areas at ambient temperatures. This is highly useful for any MEMS or lab-on-a-chip devices, which contain heat-sensitive components such as polymeric structures or coatings, antibodies, or other biomolecules or sensitive metallic structures. The method may be scaled down to bond individual chips as small as ~5.5 mm in diameter while keeping 1.4 mm diameter regions cold. Even smaller dimensions are possible with thinner silicon and Pyrex. Cavities up to ~45 µm deep may be used in the existing setup, while still keeping the reactor temperature below 100 °C. Finally, it should be possible to locally cool multiple areas/chips simultaneously when bonding whole wafers.

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Gas-phase photocatalysis in \(\mu\)-reactors

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\textbf{A B S T R A C T}

Gas-phase photocatalysis experiments may benefit from the high sensitivity and good time response in product detection offered by \(\mu\)-reactors. We demonstrate this by carrying out CO oxidation and methanol oxidation over commercial TiO\(_2\) photocatalysts in our recently developed high-sensitivity reactors. We demonstrate that the system exhibits great versatility in terms of photocatalyst, illumination source and target reaction.

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1. Introduction

Photocatalysis is the conversion of chemicals to other chemicals over a semiconducting catalyst which is activated by band-gap excitation as opposed to conventional catalysis where reactions are thermally activated. Photocatalysis may be used for elimination of unwanted chemicals such as pollutants in air or waste water by mineralizing, e.g. organics down to CO\(_2\) and H\(_2\)O\([1–3]\). The second main use of photocatalysis is (solar) energy harvesting since a photocatalyst, unlike a thermal catalyst, may convert reactants to products of higher energy thereby storing some of the energy from the absorbed photons in chemical bonds\([4]\).

The merits of \(\mu\)-reactors in the study of catalysis have been broadly demonstrated\([5–7]\), but only comparatively little work has been done to use the benefits of \(\mu\)-reactors in the study of photocatalytic reactions\([8–11]\). We have recently reported the development of a new \(\mu\)-reactor fabricated in silicon and sealed with a Pyrex lid\([12]\). Compared to previously published photochemical “micro”-reactors which typically are based on one or more channels of 10–1000 \(\mu\)m in depth and width\([10]\) our reactors are quite different with their large frontal area combined with their very shallow chambers (3 \(\mu\)m depth) and resulting small volumes. This new design features a large frontal area of 0.78 cm\(^2\) – useful for photocatalyst illumination – while keeping the total reactor volume down to \(\sim\)240 nl giving very short time constants and high sensitivity due to the integrated direct quadropole mass spectrometer (QMS) interface. In this paper we demonstrate that these \(\mu\)-reactors can be very useful in characterizing photocatalysts.

Focusing on the technique two commercial photocatalysts, P25 and W 2730X TiO\(_2\) catalysts (both from Evonik—formerly Degussa) are used to photooxidize CO and methanol. CO oxidation has previously been established as a useful probe reaction for gas-phase photocatalysis\([13,14]\) and methanol is a commonly used sacrificial reductant in photoelectrochemical studies\([2]\).

2. Experimental

The \(\mu\)-reactor system (fabrication, gas handling system, QMS detection, etc.) has been described in a previous publication\([12]\). Briefly, the reactors are planar (16 by 20 mm\(^2\) by 0.35 mm silicon (+0.5 mm Pyrex lid)) with a circular active area of 10 mm diameter and a reactor volume of roughly 240 nl. Up to four simultaneous gas streams can be led to the reactor via two inlets (I1 and I2, Fig. 1C) and the reactor effluent is led to a quadropole mass spectrometer (QMS) for detection through a capillary (which limits the reactor flow to \(\sim 10^{15}\) molecules/s) via O2. The bypass flow which never enters the circular reactor area exits via O1. This bypass flow is normally chosen to be on the order of 10 sccm to get good regulation using off-the-shelf mass flow controllers.

Fig. 1A and B are cross-sections of the \(\mu\)-reactor showing the two basic ways photocatalyst may be loaded into the reactor and that...
though Pyrex starts absorbing light at the violet end of the 0.5 mm Pyrex lids used to seal our reactors in Fig. 3. Even though the light is lost passing through the Pyrex lid due to reflection and absorption for the deeper UV we include the transmittance spectrum and intensity is recorded by replacing the reactor with a fiber bundle terminated with a collimating optic. In the present paper we excite the photocatalysts using a small 4 W Hg lamp (UVP model UVGL-15). Regardless of the light source used the incident spectrum before measurements begin. The catalyst is deposited on the glass lid is that it may be characterized by transmission UV–vis spectroscopy before measurements begin. The lamp can be used in “short” wave mode (solid, red curve) and in “long” wave mode (dashed, blue curve). In the “short” wave mode the spectrum is dominated by the narrow Hg-line at 253.6 nm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

For the experimental examples presented in this paper the P25 and W 2730X photocatalysts are loaded onto the Pyrex lids which are subsequently bonded to the silicon reactors. This corresponds to sketch B of Fig. 1 and the photocatalyst is effectively illuminated from “behind”. One advantage of depositing the photocatalyst on the glass lid is that it may be characterized by transmission UV–vis spectroscopy before measurements begin. The catalyst is deposited by spin coating. The suspension is made by sonication and the Pyrex area for deposition (circular, 8 mm diameter) is masked by “Blue Tape” (SWT20, Nitto Scandinavia AB). The thickness of the catalyst layer is controlled by the concentration of the suspension and the number of depositions in the spin coater. Once the catalyst is deposited (and possibly characterized by UV–vis or other techniques) the lid is anodically bonded to the reactor [15,12]. During anodic bonding the temperature of the catalyst is kept well below 100°C using a special “locally-cooled anodic bonding” method [16].

Once the reactor is bonded it is mounted in the gas manifold fixture and the target gas mixture flow is started. It takes a while for the reactor and catalyst to dry (as evidenced by the m/z = 18 signal in the QMS) and since trace water in our experience inhibits CO oxidation over TiO2, care is taken that the chip is dry before experiments are started. Sometimes cycles of illumination and/or heating to ∼100°C are used to speed up the drying process. For methanol oxidation careful drying is not relevant since the reaction itself evolves water.

In general, the experiment consists of supplying the relevant reactant gas mixture to the μ-reactor and pulsing the light on and off while monitoring the relevant masses with the QMS. This procedure is conducted for all wavelengths and intensities of interest. Generally, illumination causes only negligible (<4 K) increase in reactor temperature, since the metallic gas manifold to which the reactor is clamped acts as a massive heat sink.

Fig. 1. Partial cross-sections of two different μ-reactors loaded in two different ways and a photograph of a μ-reactor. Sketch A shows that when photocatalyst is deposited on the silicon reactor the illumination is frontal – i.e. light is incident from the same side as the reactants – while sketch B shows that photocatalyst deposited on the Pyrex lid (as in the examples in this paper) is effectively illuminated from behind. Sketch C shows a top view of the reactor where main parts are indicated. Gas is let in via I1 and I2 and out via O1 and O2. O1 goes to a pressure controller and O2 leads from the reactor to the mass spectrometer. The location of the cross-sectional cut shown in A and B is also indicated in C.

Fig. 2. Measured irradiation on the μ-reactors from the 4 W Hg lamp used in this paper. The lamp can be used in “short” wave mode (solid, red curve) and in “long” wave mode (dashed, blue curve). In the “short” wave mode the spectrum is dominated by the narrow Hg-line at 253.6 nm. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

Fig. 3. (A) Measured absorbance and resulting transmission of a Pyrex lid. Above ∼330 nm transmission is essentially flat at 0.92. (B) Absorbance and transmission of the TiO2 samples studied measured against a blank Pyrex lid in the reference beam (A). The P25-based sample (red curves) has more absorption and scattering than the W 2730X-based sample (blue curves). The increased scattering of P25 is most pronounced at the higher wavelengths.
This method is also suited for long-term stability testing by leaving the light source on for prolonged periods before pulsing the light to measure photo activity. The setup is automated with LabVIEW (National Instruments) so that light sources, gas pressure and feed gas composition may be automatically scanned during longer experiments.

3. Photooxidation experiments

The photooxidation experiments presented in this letter serve to exemplify the method. For these experiments two reactors were prepared. Each was spin coated three times (6000 RPM, 10 s) with a 5% mass suspension in water (18 MΩ cm, “Millipore”) of P25 and W 2730X, respectively. The resulting thickness was estimated by cross-sectional scanning electron microscopy to be approximately 400 nm on average in the case of the P25 catalyst and since the tapped density of P25 according to the data sheet is 130 g/l this corresponds to an upper limit of about 400 × 10⁻⁷ × 0.42 × π cm³ × 0.13 g/cm³ = 2.6 µg of P25 in total in the μ-reactor.

3.1. CO photooxidation over P25

Oxidation of CO is, in principle, a very simple reaction: CO(g) + 1/2(O₂)(g) → CO₂(g). Fig. 4 shows time traces of the main components of the CO oxidation reaction gas: m/z = 4 (He used as internal reference), m/z = 28 (CO), m/z = 32 (O₂), m/z = 44 (CO₂). The nominal feed gas composition is 6:6:0.085 (He, O₂, CO) by volume and the total pressure is fixed at 1 bar. It is obvious from the time trace in Fig. 4 when the light is switched on and off. The reason that m/z = 44 does not drop to zero when the light is off is background reaction on the filament of the mass spectrometer—not dark reaction in the reactor. Fig. 5 shows the another experiment where the QMS is sampling mass 44 at 10 Hz and the light is toggled every 10 s. It is seen that the system reaches 90% of steady-state level in less than 2 s after the light is toggled. This high time-resolution is a key feature inherent in our μ-reactor design and allows for e.g. very fast experiments where illumination wavelength is scanned.

In order to confirm that photooxidation is indeed responsible for the signals, an experiment of heating the loaded reactors to about 100 °C in the dark was also tried, but no measurable dark activity was seen for these catalysts. As a further check, an empty reactor (without photocatalyst) was also tested and as expected this had no activity whatsoever under illumination or under heating.

3.2. Methanol photooxidation

Methanol oxidation is slightly more complicated (and interesting) than CO oxidation. For instance it may be oxidized completely (mineralized): CH₃OH(g) + (3/2)O₂(g) → CO₂(g) + H₂O(g). Or it may oxidize partially to methanol (“formaldehyde” – CH₂O) or to methanoic acid (“formic acid” – HCOOH). In order to carry out the methanol photooxidation experiments a bubbler made of stainless steel filled with 2 ml of HPLC-grade methanol (Sigma–Aldrich) was inserted after one of the four MFCs supplying gas to our μ-reactor. The concentration of methanol is then conveniently adjusted by the ratio of clean helium to methanol-saturated helium (at the bubbler temperature which is monitored) controlled by the two corresponding MFCs. For the measurements presented in Figs. 6 and 7 the nominal ratio of partial pressures in the feed are 6:6:0.085 (He, O₂, MeOH) corresponding to about 0.7% volume of methanol. An experiment with about five times higher methanol concentrations was also tested, but resulted in a similar turnover as estimated by the m/z = 44 signal and is omitted here. For all experiments the methanol signal is monitored by the strongest feature in the cracking pattern at m/z = 31.

Figs. 6 and 7 both show methanol oxidation data, but with P25 and W 2730X and long and short wave illumination, respectively. The data clearly demonstrates that the photooxidation of methanol under these conditions takes much more time to reach...
steady state when the light is toggled than it does with CO oxidation. The methanol signal and particularly the water signal both take many minutes to fully respond when the light is toggled. Another clear feature of the data is the apparent photo-desorption (and re-adsorption) of methanol when the light is toggled although it is less pronounced than with the W 273X0 reactor (Fig. 7). This phenomenon can only be resolved thanks to the fast time-resolution of the \( m/z \) reactor so even for this (somewhat slow to reach steady state) reaction the time-resolution is a useful feature.

A mass scan from \( m/z \) 1–50 was also carried out to look for other (by)products and intermediates of methanol oxidation (such as formic acid), but nothing (that could not be assigned to cracking of water, methanol or CO\(_{2}\)) was detected in noteworthy concentration.

### 4. Discussion

As illustrated by the examples of the previous section, the \( \mu \)-reactor presented here is a versatile tool for characterization of photocatalytic performance. We show data for CO oxidation and methanol oxidation, but other reactions such as methane oxidation and ethanol oxidation have also been performed successfully. At present, experiments must be carried out in the gas-phase, but we are working on a liquid-capable version of the \( \mu \)-reactor which would be suited for e.g. water-splitting experiments.

Compared to conventional, macroscopic batch reactors (generally hundreds of milliliters in volume and employing gas chromatographic product detection) the \( \mu \)-reactors are fundamentally different. The internal volume is smaller by about 106 times and this enables flow measurements instead of batch experiments. This gives a tremendous advantage in terms of time-resolution compared to batch reactors. Time-resolution is useful for studying transient phenomena (such as photoadsorption/desorption (see Fig. 6)) or recording temperature programmed desorption (TPD) spectra, but it also means that a series of measurements (e.g. the performance of a sample over a range of wavelengths—"action spectrum") can be recorded very fast (future publication).

The freedom to deposit the photocatalyst on either the Pyrex lid or the silicon reactor itself enables easy comparison between performance under frontal or back-illumination (Fig. 1). It is expected that for thin films of photocatalyst the performance should be the same regardless of illumination orientation, but for thick films, frontal illumination should give higher turnover (future publication).

Finally, the lower limit on illumination wavelength imposed by the transmission of the Pyrex lid is not really a hard limit. The optical absorption shown in Fig. 3 is for our standard lids which are 0.5 mm thick, but we have successfully "thinned" them to less than 100 \( \mu \)m in thickness by etching one side in dilute HF. This procedure results in significantly increased transmission in the 200–250 nm range making measurements on photocatalysts with a band-gap up to 6 eV practical.

### 5. Conclusion

We have shown that gas-phase photochemistry may be conveniently investigated using our silicon \( \mu \)-reactors due to the transparency of the Pyrex lids in the relevant wavelength range. We carried out mineralization of methanol as a general representative of such reactions, but in principle anything of interest that has a practical vapor pressure could be substituted for methanol in the bubbler. The photocatalytic oxidation of CO has become the "standard" test reaction in our group since it is convenient to do and has near-instant response to illumination which allows for mass-transport studies in thick, mesoporous systems.

To our knowledge, the combination of excellent time-resolution (which gives mechanistic information on absorption/desorption and mass transport) and versatile high-sensitivity detection offered by on-line QMS is far better than anything achievable with more conventional "macro" reactors with \( 10^{9} \) larger reactor volumes and gas chromatograph product detection.

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### References

Quantitative measurements of photocatalytic CO-oxidation as a function of light intensity and wavelength over TiO$_2$ nanotube thin films in $\mu$-reactors

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Abstract

Gas-phase photooxidation of CO over TiO$_2$ catalysts (P25 and TiO$_2$ nanotubes) in $\mu$-reactors with quantitative product detection was used to study turnover as a function of illumination intensity over four orders of magnitude. Turnover was found to be of order 0.84 in illumination intensity. A CO photooxidation action spectrum was also recorded for TiO$_2$ nanotubes. The action spectrum was used to calculate both the Incident Photon to Product Efficiency (IPPE) and the Absorbed Photon to Product Efficiency (APPE). The wavelength dependence of the IPPE was found to follow the absorption spectrum while the APPE was found to have a peak around 345 nm with a value of about 0.8%.

1 Introduction

In photoelectrocatalysis, it is a well established practice to measure photocurrent to estimate activity. Provided, that it can be proved which reaction takes place at the photoelectrode and counter electrode (e.g. evolution of oxygen and hydrogen in the common case of water splitting), the current measured by the potentiostat gives a highly sensitive and convenient measure of photoactivity. However, in the case of photocatalysis where chemicals are converted into other chemicals on the photocatalyst surface the absence of external current makes it much more problematic to quantify the photocatalytic activity. For both liquid and gas phase reactions it is necessary to quantify product molecules which is much harder than measuring a current. The problem of product detection is particularly difficult when e.g. the activity dependence on wavelength (action spectrum) is sought. Many wavelengths must be tested to give a reasonable resolution in the action spectrum, and monochromatic light sources tend to be weaker than broad band light sources. In practice, this often makes measurement of action spectra very time consuming.

In this paper, we demonstrate how our $\mu$-reactor system presents a novel and superior alternative to the traditional approach to such measurements. The traditional procedure is to place a macroscopic amount (1 to 1000 mg) of photocatalyst in a macroscopic (batch)reactor (1 to 1000
ml) made of glass, quartz or metal and use a gas chromatograph (GC) to analyze small samples of the reactor content at suitable time intervals under illumination.\textsuperscript{1,2} Some groups even employ reactors of several liters and other detection schemes (e.g. photoacoustic).\textsuperscript{3,4} Other groups use flow (single pass) reactors, but these are also typically larger than 100 ml.\textsuperscript{5}

Some groups have studied photocatalysis in small (mm size) flow-reactors,\textsuperscript{6–9} and our group has recently developed a \( \mu \)-reactor with quadropole mass spectrometer (QMS) detection\textsuperscript{10} and shown its suitability for (thermal) heterogeneous catalysis as well for as photocatalysis.\textsuperscript{11} In the following we present:

- How quantitative photocatalytic experiments may be carried out using our \( \mu \)-reactor platform.
- How the large dynamic range of the reactor and QMS detector allows fast studies of photocatalytic turnover rate as a function of illumination intensity over 4 orders of magnitude and discuss how the results relate to the literature.
- How the \( \mu \)-reactor system can be used to record a detailed action spectrum of a photocatalyst in an automated fashion in only 2 hours and calculate quantum efficiencies (Incident Photon to Product Efficiency - IPPE) and (Absorbed Photon to Product Efficiency - APPE).

## 2 Quantitative measurements in \( \mu \)-reactors

### 2.1 The \( \mu \)-reactor

There is no general consensus about what the term \( \mu \)-reactor covers. We use the term to cover “chemical reactors with dimensions in the \( \mu \)m range”. The general merits of such systems have been demonstrated by other groups.\textsuperscript{12,13} Our \( \mu \)-reactors seen in Figure 1 (described in detail elsewhere\textsuperscript{10}), briefly, are 16 by 20 mm\(^2\) chips fabricated from 350 \( \mu \)m thick silicon substrates and permanently sealed with a 500 \( \mu \)m thick Pyrex lid using anodic bonding\textsuperscript{14} with local cooling of
the catalyst (the catalyst is kept well below 100°C during bonding). Each chip contains a circular reactor area of 0.78 cm² yet it has a total volume of only 240 nl (3 μm depth). Gas is continually led from the reactor area via a flow-limiting capillary to a QMS (Balzers model QMA125 with axial ionization and a secondary electron multiplier (SEM) detector) for instantaneous detection. This combination of a large area for illumination, with a fast time response (of this flow reactor) and a high sensitivity, makes the μ-reactor well suited for gas-phase photocatalytic studies. Two kinds of chips with different capillary widths are available. These have an order of magnitude different flow conductance so that the flow through the reactor can be either ~5 × 10¹⁴ or ~5 × 10¹⁵ molecules/s depending on the experiment. The gas source, which feeds the reactor with this tiny flow, is the bypass flow channel. This can accommodate up to 20 ml/min enabling conventional mass flow controllers to be used for gas supply and the reactor flow is independent of the main channel flow (it depends only on the main channel pressure which is fixed by a pressure controller within the useful range 0.05 to 5 bar). In the experiments, presented in this paper, the pressure is fixed at 1.00 bar and the feed gas composition is 3:3:1 (He:O₂:CO) by volume.

Figure 1: Photograph of a μ-reactor. I₁ and I₂ are gas inlets and O₁ is the outlet for the bypass flow. A small amount of gas (5 × 10¹⁴ or 5 × 10¹⁵ molecules/s depending on the type of reactor) is continually drawn from the reactor area via the flow-limiting capillary through O₂ to the mass spectrometer for detection.

In this study, the samples are prepared by depositing the photocatalyst on the Pyrex lid (of the μ-reactor) before it is bonded onto a silicon chip to complete the loaded μ-reactor. The sample
The μ-reactor is then mounted in a gas manifold fixture and the reactant gas mixture flow is started. The μ-reactor is subsequently heated to $\sim 100^\circ$C, until it is completely dry as evidenced by the water signal at $m/Z = 18$, and no experiments are carried out before the water signal has reached a steady background level and the photoactivity has stabilized. This is important, because we have found photooxidation of CO to be inhibited by water as was also reported by Einaga et al.\textsuperscript{16}. In general, once the samples have been mounted and dried, the photocatalytic performance is very stable over time and reproducible - even if the reactor is dismounted and then remounted months later. Since the μ-reactor is a flow-reactor the typical experiment consists of toggling a light source on and off while recording all relevant masses with the QMS as a function of time (equivalent to measuring a photocurrent under chopped light).

2.2 Calibration procedures

The raw data obtained from the μ-reactor setup consists of time series of currents - one for each $m/Z$-value being scanned. What is sought, is the ability to convert from measured QMS currents to molecular flows (Ampere $\rightarrow$ molecules/s). There are four steps to perform to convert from QMS currents to molecular flows, but step 1 must, in principle, only be done once and then only steps 2-4 (which are very quick) have to be performed with every new μ-reactor:

1. Measure the molecular flow of a “reference” μ-reactor by pumping down a known volume fitted with a baratron through the capillary of the reference μ-reactor. Call this flow $R_{flow}$. The unit is [molecules/s]. The details of this procedure may be found in.\textsuperscript{10}

2. Find the molecular flow of the sample μ-reactor, $S_{flow}$ [molecules/s]. This is conveniently done by comparing the QMS current of a suitable gas component (this \textit{inert} internal reference is typically He measured at $m/Z = 4$) of the sample μ-reactor with the reference μ-reactor using the same gas mixture. This gives the relation

$$S_{flow} = R_{flow} \frac{S_{QMS(inert)}}{R_{QMS(inert)}}$$

(1)
where \( \frac{S_{QMS(\text{inert})}}{R_{QMS(\text{inert})}} \) is the ratio of measured QMS currents [Ampere/Ampere] of the inert gas in the sample \(\mu\)-reactor to the reference \(\mu\)-reactor. This simple method of swapping the sample with the reference reactor is much faster and more convenient than doing a pump-down experiment (step 1) with every sample \(\mu\)-reactor.

3. Measure the QMS signal for every interesting component, \( n \), in a known gas mixture to find a set of calibration constants, \( C_n \), (sensitivity factors):

\[
C_n = \frac{S_{\text{flow}}}{S_{QMS}(n)}
\]

(2)

where \( f(n) \) is the fraction of the \( n \)th component of the gas (\( \sum f(n) = 1 \), where summation is over all components) and \( S_{QMS}(n) \) is the QMS current measured for the \( n \)th component. Each calibration constant is the ratio of the molecular flow to the measured QMS current of a given gas, \( n \). They capture differences in ionization probabilities etc. In general, calibration constants are almost equal to each other (within 50%) - except for He which has a low ionization cross section.

4. Now the molecular flow of each gas component, \( n \), is given by

\[
S_{\text{flow}}(n) = C_n S_{QMS}^b(n)
\]

(3)

where \( S_{QMS}^b(n) \) is the QMS signal that has been corrected for background in the QMS (including cracking and reaction on the filament). In the case of CO (photo)oxidation this is easy, since there is no reaction in the dark (verified in separate experiments), so the dark \( \text{CO}_2 \) signal (m/Z = 44) is the background and in the above equation \( S_{QMS}^b(\text{CO}_2) = S_{QMS}(\text{CO}_2) - S_{QMS-\text{dark}}(\text{CO}_2) \)

The order of magnitude for molecular chip flow \( (S_{\text{flow}}) \) is \( 5 \times 10^{14} \) molecules/s - i.e. \( 10^{-9} \) moles/s for \(\mu\)-reactors with the small capillary and \( \sim \)10 times higher for \(\mu\)-reactors with the large capillary.
Implicit in the calibration is the assumption that the QMS is linear (i.e. a 10 times reduction in pressure of a given gas component in the QMS results in a signal that is exactly 10 times lower). A linearity calibration of the mass spectrometer has been carried out and we have no reason to suspect any non-linearity leading to a systematic instrumental error. We also note, that we generally see mass balance for carbon and oxygen: \( \text{CO} + \text{CO}_2 = \text{constant} \) and \( 2\text{O}_2 + \text{CO} + 2\text{CO}_2 = \text{another constant} \).

3 Samples and sample preparation

Sample “A” was simply P25 (AEROXIDE P25, Evonik (formerly Degussa)) spin coated in a masked 8 mm disc on a Pyrex lid by the method given in.\(^{11}\) The resulting film thickness was estimated to be \(225 \pm 25\, \text{nm} \) by SEM on similarly prepared samples. The lid was then bonded (as explained in section 2) to a wide-capillary silicon chip to complete the \(\mu\)-reactor.

Sample “B” consisted of an 8 mm diameter disc of \(\text{TiO}_2\) nanotubes (\(\text{TiO}_2\) NTs) formed on the Pyrex lid by potentiostatic anodization of a metallic titanium film\(^{17,18}\) (400 nm thick, 8 mm diameter) which was deposited on the Pyrex lid using electron beam evaporation. \(\text{TiO}_2\) NTs have attracted much attention in recent years\(^{19}\) due to their favorable combination of photocatalytic performance and mass transport properties. Prior to anodization, the samples were cleaned with acetone and ethanol followed by a deionized water rinse. The anodization was performed using a two-electrode cell with the titanium film as the working electrode and carbon paper as the counter electrode. The anodization was complete within \(\sim 1\, \text{hour} \) at a constant applied voltage of 10 V at room temperature in an electrolyte mixture of 0.3\%\text{mass} \text{NH}_4\text{F} (98\% + \text{ACS reagent, Sigma Aldrich}) and 2\%\text{volume} \text{H}_2\text{O} in ethylene glycol (99\%, Sigma-Aldrich).\(^{20}\) In order to get complete anodization without loss of electrical contact the so-called “bottom contact” method\(^{21}\) was used. After growing the \(\text{TiO}_2\) NT film the lid was annealed in a furnace at 723 K for 2 hours. The resulting film consisted of ordered arrays of nanotubes of about 400 nm length (thickness of the
film) ∼30 nm in outer diameter and ∼20 nm in inner diameter (estimated from scanning electron micrographs of similarly prepared samples). X-ray diffraction (XRD) peaks in the annealed film were all assigned to anatase, but of course XRD cannot rule out that some TiO$_2$ might remain amorphous after annealing.$^{22}$

Figure 2: Absorbance ($A = \log(I_0/I)$) of sample “B” - red plus signs, left ordinate - measured against a blank Pyrex lid in the reference beam. The black curve is a fit ($A_{\text{scattering}} = C_1/\lambda^4 + C_2$) to the data above 400 nm as a simple model of the scattering losses. Subtraction of the fit from the absorbance is plotted with blue crosses and represents the “scattering corrected” absorbance. The right ordinate is the resulting absorption ($1 - I/I_0$) - red and blue solid curves. Again, the blue curve is the “scattering corrected” data. The inset shows a close-up of the band edge region. For instance it can be read off the blue curve that only below 385 nm does the nanotube film absorb more than 2% of the incident photons. Scattering (black line) is probably overestimated at short wavelengths since scattered photons have a high absorption probability due to short absorption length, but the error due to this is insignificant since raw and corrected absorbance remain essentially equal at short wavelengths (both above 95%).

Figure 2 shows the UV-VIS spectrum of the TiO$_2$ NT sample “B” measured (with a Cary model 1E spectrophotometer) against a blank Pyrex lid. Thus, the resulting apparent absorption is only due to absorption and scattering of the TiO$_2$ film - the absorption due to the Pyrex itself is therefore not contributing to the measured absorbance in the figure. Figure 2 also shows a fit of the scattering background of the form $A = C_1/\lambda + C_2$, where $C_1$ and $C_2$ are fitted using the Levenberg-Marquardt method. (Since the characteristic feature size ($r \lesssim 30$ nm) for both P25 and TiO$_2$ NTs then $2\pi r/\lambda << 1$ for $\lambda > 400$ nm and thus Lorentz-Mie scattering reduces to Rayleigh scattering
in a first approximation.) The scattering was fitted in the (near) above-gap region 400 nm to 600 nm (3.1 eV to 2.07 eV) since the anatase nanotubes have a band gap, $E_g \approx 3.2$ eV. Figure 2 shows the resulting “corrected” absorption data for the sample (where the fitted scattering component has been subtracted). The scattering correction will be needed for the discussion of Absorbed Photon to Product Efficiency and action spectra (section 6). After UV-VIS characterization the lid was bonded to a narrow-capillary silicon chip. The samples both have the photocatalyst sitting on the glass lid so they are both illuminated “from behind” with respect to the reactant gas mixture flowing through the reactor as explained elsewhere.  

4 Light sources

Two very different light sources are used in this work. The first is a high-power UV-LED source (Hamamatsu model LC-L2) fitted with a focusing lens assembly (Hamamatsu L10561-220) suited for areas of 8 mm in diameter. The peak wavelength is $\sim 367$ nm and the FWHM is $\sim 9$ nm. In our setup an average irradiance on the sample $\mu$-reactor of $\sim 645$ mW/cm$^2$ at full power was measured using a calibrated spectroradiometer (International Light model RPS-900R). The LED unit may be electronically tuned down to 10% of full power. Combination with simple neutral density (ND) filters of optical density 1.0 and 2.0 (Newport corp.) makes a few extra orders of magnitude in light intensity available. A range of combinations of filters and power settings were measured using the spectroradiometer to calibrate for the exact extinction of the individual ND filters (which at 367 nm is not exactly equal to their nominal values).

The second light source is shown in Figure 3. The main components include an (ozone free) 1 kW Xe-arc source (Newport model 66924) equipped with a water filter to eliminate unwanted long-wave light and for this study it was fitted with a monochromator (Newport Cornerstone 260) and appropriate optics for F-number matching. The output is coupled via a quartz fiber bundle.
Figure 3: Schematic of the monochromated Xe-arc source used for measuring action spectra. The irradiance of the system at all relevant settings (choice of wavelength, slits and grating) is measured by putting the measuring head of a calibrated spectroradiometer in the place of the $\mu$-reactor. This irradiance measurement is carried out immediately before or after the actual measurement on the $\mu$-reactor.
through a collimating lens onto the sample $\mu$-reactor.

The $\mu$-reactor and catalyst is kept at room temperature in all experiments since the $\mu$-reactor is clamped to a metallic gas interface manifold which acts as a heat sink ($\Delta T < 4$ K at full power illumination$^{11}$).

5 Intensity dependence

5.1 Motivation

The high sensitivity of the $\mu$-reactor system which enables flow experiments where steady state conditions can be ensured is a great advantage compared to batch reactors. This merit, in combination with the fact that the QMS offers a very wide dynamic range (ratio of minimum detectable signal to maximum practical conversion which is limited by “full conversion”), makes the $\mu$-reactor platform highly suited for investigations of how the photocatalytic conversion scales with illumination intensity. It is of interest to know how well a given photocatalyst performs as a function of illumination intensity for at least three reasons. The first reason is practical: In a given photocatalytic converter where higher conversion is needed, would it be more economical to increase photocatalyst amount/surface area - or would a more powerful light source with the same amount of photocatalyst be the better choice? The second reason is that when trying to characterize the photocatalytic performance as a function of illumination wavelength (action spectrum) it may be important to correct measured turnover for intensity variation when the tunable light source does not provide the same irradiance at different wavelengths. For example, when using an Xe-arc lamp with a monochromator to record action spectra, as is commonly done in many labs and as we do in section 6, the irradiance on the sample will often vary by an order of magnitude (or more) as the wavelength is scanned, so that, effectively, two parameters (wavelength and irradiance) are scanned simultaneously; if the turnover is not linear in irradiance for a given sample, then the action spectrum must be corrected for that. The third reason for measuring intensity dependence is that it
gives mechanistic insight about the sample. For example, it is often claimed that in the limit of low light intensity (where mass transport is not a limiting factor) turnover should scale linearly with incident photon flux. Furthermore, it is claimed that at higher irradiance levels turnover becomes proportional to \((\text{irradiance})^{0.5}\) due to substantial carrier recombination. Experimental support for this was found by Egerton and King\(^{23}\) by oxidizing isopropanol to acetone over rutile TiO\(_2\) and commercial pigments in the liquid phase while varying irradiance over five orders of magnitude. Later, however, Ohko et al.\(^1\) studied the same reaction in gas phase over a TiO\(_2\) thin film at very low light intensities (45 \(\mu\)W/cm\(^2\) down to 36 nW/cm\(^2\) - the latter corresponding to only \(6.6 \times 10^{10}\) photons/(cm\(^2\)s)) and found (as long as the isopropanol concentration was above 10 ppmv) turnover to be proportional to \((\text{irradiance})^{0.8}\) over their 3.5 orders of magnitude in irradiance.

Given that our \(\mu\)-reactor setup uses a mass spectrometer (as opposed to a gas chromatograph) for detection and that one should always choose to use probe reactions with a well defined stoichiometry\(^{22}\) we have chosen photooxidation of CO. Photooxidation of CO has previously been established as an interesting probe reaction for photocatalysis over TiO\(_2\). It has been studied over single crystals at low temperatures\(^{24}\) and over powders at room temperature.\(^{16,25}\) For pure TiO\(_2\), Einaga et al.\(^{16}\) observe that water vapor inhibits photooxidation of CO. We have also observed this inhibiting effect\(^{11}\) and therefore take great care to dry our reactors until activity is stable before performing any measurements as explained in section 2. In addition to pure TiO\(_2\), references\(^{16,24,25}\) also study platinized TiO\(_2\), and in the case of Einaga et al.\(^{16}\) also the effect of water vapor and of light intensity, and find that platinized systems are less sensitive to water than plain TiO\(_2\) is.

### 5.2 Results

In order to be able to study illumination intensity dependence over a large range of intensities we have used our Hamamatsu LED unit (section 4) because it is fairly monochromatic at 367 nm and that it can provide a high irradiance over the reactor area.
Two $\mu$-reactors, “A” with P25 and “B” with TiO$_2$ NTs (section 3) were used for the experiments. For both samples, the light intensity is almost constant over the thickness of the sample because the photocatalyst layers are very thin and because of the proximity of the 367 nm central wavelength to the band edges. Especially for the nanotube $\mu$-reactor its absorption edge is at $\sim$380 nm so in simple transmission only about 10% is absorbed at 365 nm (see Figure 2). This means that for both samples the excitation rate should be approximately constant everywhere in the photocatalyst layers. Figure 4 shows data for measured CO$_2$ production (measured as the m/Z

![Figure 4: Background-corrected m/Z = 44 (CO$_2$) QMS signal as a function of measured irradiation on the reactor with $\lambda = 367$ nm peak wavelength. For the nanotube $\mu$-reactor (sample “B”) it is seen that, except for the highest illumination intensities where the effective feed gas composition is altered by high turnover in the reactor (final two data points where well over 10% of the CO is photooxidized to CO$_2$), the turnover vs. illumination intensity is very well described by a power function. The apparent slope (power) is 0.84 meaning that a doubling of the light intensity only results in a factor 1.79 times more turnover. This relation holds true over four orders of magnitude of light flux - from moderate to very high flux (90 $\mu$W/cm$^2$ to 645 mW/cm$^2$ = $1.7 \times 10^{14}$ to $1.2 \times 10^{18}$ photons/(cm$^2$ s)). Also in the case of P25 (sample “A”) it seems that the turnover is proportional to illumination intensity to the power of about $\sim$0.84. At intensities above $\sim$5 mW/cm$^2$, however, the power law fails (or changes to a lower power), but it cannot be ruled out that this is due to transport limitations in the P25 film.

= 44 QMS current where the constant background signal has been subtracted) as a function of measured irradiance (centered at 367 nm) for the two different $\mu$-reactors from 90 $\mu$W/cm$^2$ to 645 mW/cm$^2$. For comparison, integration of the AM1.5G spectrum (ASTM G173-03 solar spectrum) in the 10 nm interval from 365 to 374 nm gives 0.67 mW/cm$^2$. The data are presented in a log-log plot so if turnover were proportional to illumination intensity the data would fall on lines.
of slope 1. For the nanotube \(\mu\)-reactor, it is remarkable that the turnover vs. intensity falls on a straight line over four orders of magnitude (of course as a substantial fraction of the available CO is converted in the final couple of data points the linearity fails). Turnover is not proportional to irradiance (slope \(\neq 1\)), but rather to irradiance raised to the 0.84 power (the reaction is of order 0.84 in irradiance). For P25, the same slope is seen at moderate irradiance up to about 1 mW/cm\(^2\), but above 5 mW/cm\(^2\) the slope is lower. This could be due to a change in mechanism, but it could just as well be due to transport limitations.

To ensure that the slope of 0.84 is not somehow an artifact of the illumination wavelength being close to the band edge a similar experiment (not shown) was conducted with a mercury lamp at 254 nm (strong line in the Hg spectrum) with the nanotube sample, although the illumination could only be varied over one order of magnitude for practical reasons. The result under those conditions of much higher photon energy was that the turnover seemed proportional to irradiance to the 0.75 ± 0.06 power.

### 5.3 Discussion

As mentioned in the above motivation the non-linearity of photocatalytic conversion in irradiance for CO oxidation and other gas (and liquid) phase photocatalytic reactions over TiO\(_2\) have previously been reported in literature. Peral and Ollis\(^{26}\) note for acetone oxidation in gas phase that \(r \propto I^{0.7 \pm 0.1}\) (\(I\) is irradiance and \(r\) is rate) over one order of magnitude and conclude that they are in the “transition regime” between the values of 0.5 (recombination dominated) and 1.0 (light limited). Aguado et al.\(^{27}\) report that for one of three different colloids they test for formic acid decomposition in liquid phase they find that \(r \propto I^{0.78 \pm 0.2}\) (the two other colloids have even lower exponents). Einaga et al.\(^{16}\) studying CO oxidation at high light intensities (\(\sim 1\) to 10 W/cm\(^2\)) find that \(r \propto I^{-0.7}\) for TiO\(_2\) (and \(r \propto I^{-0.5}\) for platinized TiO\(_2\)). Hwang et al.\(^{28}\) find \(r \propto I^{0.73 \pm 0.1}\) for CO oxidation over platinized TiO\(_2\) (\(\sim 0.03\) to 3 mW/cm\(^2\)). Even Ohko et al.\(^1\) who measure isopropanol oxidation in the gas phase over three orders of magnitude at what they call “Extremely low” light
intensities and arrive at \( r \propto I^{0.8\pm0.04} \) conclude that they are in a “transition region” between the two asymptotic values.

Considering that Ohko et al.\(^1\) measure \( r \propto I^{0.8\pm0.04} \) with \( I \) from 36 nW/cm\(^2\) to 45 \( \mu \)W/cm\(^2\) and that we measure \( r \propto I^{0.84\pm0.03} \) with \( I \) from 90 \( \mu \)W/cm\(^2\) to 645 mW/cm\(^2\) (albeit for a different kind of TiO\(_2\) film and a different reaction) it seems unreasonable that the combined seven orders of magnitude in light intensity where \( r \propto I^{-0.8} \) is just a “transition region” between the low light limit where supposedly \( r \propto I \) and the recombination dominated region where supposedly \( r \propto I^{0.5} \). A related question is whether anyone has really ever measured \( r \propto I^{1.0} \).

Egerton and King\(^2\) show that only one pigment (out of the three commercial pigments plus rutile that they test) shows \( r \propto I^1 \) at low light intensities, and this conclusion is based on only two data points - the rest of the data for that pigment at higher intensities shows \( r \propto I^{-0.5} \) as does the data for the other two pigments. We hesitate to conclude that turnover can never be truly proportional to incident photon flux, but it appears that it is hard to find a (TiO\(_2\)-based) photocatalyst and a probe-reaction where this can be measured in practice.

6 Action spectra

Another great benefit of the fast response and low detection limit offered by the \( \mu \)-reactor platform in photocatalysis is the collection of action spectra. “Chemical”, photocatalytic action spectra are useful and complement traditional “electrical”, photoelectrocatalytic action spectra. This is because reactivity is measured under true zero-bias conditions without the influence of the solid-liquid junction on band structure and without possible artifacts due to non-Faradayic photocurrent.

Most tuneable and monochromatic sources provide only modest irradiation levels, thus the measurement of photocatalytic action spectra with traditional large volume (batch) photoreactors
and gas chromatographic product detection can take many hours of illumination to obtain a quantifiable product concentration at every wavelength. This long time scale can complicate the measurements due to adsorption of both reactants and products during the measurement - not least because of the unfavorable ratio between active catalyst area and reactor inner surface area that is typical of large reactors. In the case of the μ-reactor the same measurement can be quite fast because the μ-reactor has sufficient sensitivity that flow-experiments are possible. In this section, we present an action spectrum for the TiO$_2$ nanotube sample “B” measured from 290 nm to 400 nm in 5 nm intervals - all recorded in 135 minutes using an automated LabVIEW program.

The raw measurements of the monochromated output of the Xe light source at every wavelength used in the study are presented in Figure 5 (for a description of the light source, see section 4). With this instrumental configuration the FWHM is on the order of 9 nm and the peak irradiance is around 40 μW/(cm$^2$nm) for central wavelengths in the relevant range (∼300 - 370 nm). As a reference, AM1.5G is also shown in Figure 5 and it is seen that its irradiance is of the same order of magnitude as the monochromator output. No effort was made to keep irradiance constant over the wavelength interval. Given the results from the previous section such extra refinements might be relevant for highly accurate characterization, but for the purpose of demonstrating the technique it was considered unnecessary - not least because irradiance is constant to within a factor of two in the 310 nm to 370 nm interval.

For photon-to-product molecule efficiency calculations it is the number of incident photons (not incident power) that is the relevant parameter. The conversion, photon flux = power flux/(photon energy), has been carried out and the result is plotted in Figure 6 which also includes the integrated photon flux density for every monochromator setting in units of photons/(cm$^2$s). The light output from the monochromator is moderate - for example at 350 nm the integrated flux density of $6 \times 10^{14}$ photons/cm$^2$s which corresponds to 325 μW/cm$^2$ (Figure 6).
Figure 5: Irradiance spectra measured at the μ-reactor surface for all the monochromator settings used for recording action spectrum. For clarity, every other wavelength measurement (290, 300, 310, ...) is plotted with solid, red and every other wavelength (295, 305, 315, ...) in dashed, blue. Note that in the wavelength interval (310 to 370 nm) the irradiance is constant within a factor 2. AM1.5G (dotted, black line) is included for comparison.

Figure 6: Data from Figure 5, but converted to photon flux density (instead of energy flux density). The green squares show the integrated photon flux density at each monochromator setting (second ordinate). This flux density is on the order of $5 \times 10^{14} / (\text{cm}^2 \text{s})$ in the relevant wavelength range < 375 nm.

Having calibrated photon fluxes, the next step is to mount a μ-reactor and measure turnover at each monochromator setting. The resulting time trace of the m/Z = 44 signal (CO$_2$) is plotted in Figure 7. In this case the light is on for six minutes, off for six minutes and the wavelength is changed every 12 minutes. Raw data such as those shown in Figure 7 may be converted to more useful units of CO$_2$ molecules/s vs. wavelength by applying the QMS calibration procedure explained in section 2. Applying this calibration, and taking an average figure for CO$_2$ turnover at each wavelength gives the data presented in Figure 8. This figure shows the calibrated CO$_2$ turnover at every wavelength and, for convenience, also integrated incident photons/s and the estimated number of absorbed photons at each monochromator setting (both right ordinate). The integrated number of incident photons is, of course, simply the data from Figure 6 multiplied by the geometric area of the photocatalyst in the μ-reactor - in this case $\pi(0.4 \text{ cm})^2 = 0.50 \text{ cm}^2$. The number of absorbed photons is calculated as the incident photons multiplied by the probability that a photon (which has made it through the Pyrex lid) is absorbed: $\Phi_{\text{abs}} = \Phi_0 (1 - P_{\text{Pyrex}}(\lambda)) P_{\text{Sample}}(\lambda)$,
where $\Phi_0$ is the incident light flux, $P_{\text{Pyrex}}(\lambda)$ is the fraction of photons absorbed by the 500 $\mu$m thick Pyrex lid, and $P_{\text{Sample}}(\lambda)$ is the probability that a photon (which reaches the sample) is absorbed by the sample. $P_{\text{Sample}}(\lambda)$ is estimated as the “scattering corrected” absorbance of the TiO$_2$ film as explained in section 3 and $P_{\text{Pyrex}}(\lambda)$ (which includes reflection losses) is found by measuring a blank Pyrex lid in the spectrophotometer. (The Pyrex lid transmits $> 90\%$ down to about 330 nm and $\sim 80\%$ at 290 nm.$^{11}$) The only step left to get an action spectrum is to divide the CO$_2$ production by the photon count at every wavelength (and possibly by an intensity correction term if $r \not\propto I^1$ (see section 5) and if the output from the monochromator varies a lot (e.g. 10x) over the wavelength interval).

The result is shown in Figure 9 (no intensity correction) which shows the Incident Photon to Product Efficiency (IPPE) as well as the Absorbed Photon to Product Efficiency (APPE). The IPPE - the apparent quantum yield - is really the photocatalytic (chemical) equivalent of the photoelectrocatalytic (photocurrent, IPCE) action spectrum. For the catalyst tested here it takes about 220 incident photons (of $\lambda \lesssim 340$ nm) to make one CO$_2$ molecule (IPPE of 0.45%). Above 340 nm the IPPE rapidly drops off, reflecting the fact that photons close to the absorption edge have a high
probability of penetrating the film without being absorbed (Figure 2). The APPE is the same as the intrinsic quantum yield except that it includes no corrective factor for the number of photons (e^- + h^+ pairs) needed for the reaction. In the present case, the APPE reaches a maximum of about 0.8% to 0.9% (corresponding to one CO_2 molecule for every \sim 120 absorbed photons) for wavelengths in the interval 330 nm to 355 nm. At lower wavelengths there is a drop-off in the APPE down to about 0.55% below 315 nm. We suspect that this is due to the decreased average penetration length of high energy photons. At 315 nm, for example, 60% of the photons are absorbed within the bottom 100 nm of the 400 nm TiO_2 nanotube film (this may be derived from the absorbance data in Figure 2) and since the sample is illuminated from the back, with the respect to the reactants, it seems reasonable that high energy photons result in less CO_2 than lower energy photons - given that they are absorbed (APPE). At 350 nm, less than 50% of the photons are absorbed by the entire 400 nm of the film so for \lambda > 350 nm, the excitation is nearly homogenous. The reason for the drop in APPE at higher wavelengths is less obvious. One possibility is that even though photons are absorbed, some may only excite localized interband states where the electron-hole pair is not free to migrate to the surface as opposed to “real” above-band gap excitation where the charge carriers have a chance to reach the surface and induce CO-oxidation. This could explain the drop in APPE above 350 nm. We note that the APPE data for \lambda = 375 nm and 380 nm have a very high uncertainty because both the numerator (turnover) and the denominator (absorbed photons) tend toward zero for higher wavelengths (Figure 8).

7 Conclusions

We have demonstrated that \mu-reactors may be a convenient alternative to macroscopic reactors for obtaining quantitative information about photocatalytic performance. Specifically, we have investigated photooxidation of CO over TiO_2 thin films (P25 and nanotubes) at room temperature and found turnover for both types of TiO_2 to be proportional to irradiance to the power of 0.84 \pm 0.03 over four orders of magnitude in irradiance (moderate to high irradiance). We have also
Figure 9: Incident Photon to Product Efficiency (IPPE) and Absorbed Photon to Product Efficiency (APPE). Up to \(\sim 340\) nm one \(\text{CO}_2\) molecule results for every \(\sim 200\) photons incident on the reactor. At wavelengths above \(\sim 340\) nm the IPPE quickly drops off reflecting the fact that many photons pass the TiO\(_2\) nanotube layer unabsorbed. Considering only the fraction of photons absorbed, the APPE, it is clear that higher wavelength may well induce turnover - up to about 380 nm. The APPE has a broad maximum at \(345 \pm 15\) nm where the efficiency is about 0.8\%. The APPE data at 290 nm and, particularly, above 370 nm is very uncertain. This is because it is calculated as conversion divided by absorbed photons and in the extremes of the plot both denominator and numerator are close to zero.

determined the action spectrum for the TiO\(_2\) nanotubes and found the Incident Photon to Product Efficiency to be almost zero above 375 nm, that it has a small peak around 330 nm and that it is almost constant below 320 nm. This corresponds closely to the (scattering corrected) absorbance of the sample. We also estimated the Absorbed Photon to Product Efficiency, which is peaked around 345 nm - a significantly higher wavelength than the IPPE.

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Photocatalytic action spectrum of TiO$_2$ nanotubes.
References


