Master thesis

Design and testing of a single catalyst particle diagnostic platform at elevated temperature and pressure

By Jeroen Vollenbroek (s1096214)

UNIVERSITY OF TWENTE
MCEC PROGRAM
EWI
BIOS-LAB-ON-A-CHIP GROUP
MASTER ELECTRICAL ENGINEERING
TIME AND DATE: 15h, 1 July 2016
REPORT NO.: 2016-17

EXAM COMMITTEE:
Prof.dr.ir. A. van den Berg
Dr.ir. M. Odijk
Dr.ir. R.M. Tiggelaar
Prof.dr. J.G.E. Gardeniers
Prof.dr.ir. B.M. Weckhuysen
INTRODUCTION AND OUTLINE
For my master thesis at the BIOS-Lab-on-a-Chip group, and as a part of the Netherlands Centre for Multiscale Catalytic Energy Conversion (MCEC) program, I was tasked with the assignment of designing and testing a ‘Single Catalyst Particle Diagnostics: Droplet Microreactor platform’. This microreactor should be able to study single catalyst particles at high temperatures. As a report I have written a paper entitled ‘Design and characterization of a microreactor for monodisperse catalytic droplet generation at elevated temperatures and/or pressures’. In this paper I will explain all the results and findings obtained so far. The title is slightly different from the title chosen for my thesis, because the actual diagnostics within a droplet have not been achieved yet. However, as I will demonstrate, a microreactor with the potential of doing exactly that has been fabricated. The paper is accompanied by a supplementary information with more details about certain design aspects mentioned in the paper. As a small background the official project description from the MCEC website is given, followed by the paper and supplementary information.

BACKGROUND
Recent studies indicate that heterogeneous catalysts vary tremendously, induced by dynamic changes in active sites both between and within single catalyst particles. Traditional characterization approaches of catalyst particles in large reactor vessels results in measurements representing ensemble averages. On the other hand, individual particle characterization is costly and time consuming and can therefore only be done on a limited amount of catalyst particles. There is a need for a single catalyst diagnostic platform to characterize single particles at low-cost and high-throughput, to enable a massive search to find and select the best catalyst particles and related synthesis formulation approaches. Droplet microfluidics can trap single catalyst particles at several thousands of droplets per second, and allows to graft, react, and analyse each particle individually. The most promising particles can be selected for further in-depth analysis. Ultimately, the knowledge obtained from this research project will help to improve catalyst particles for use in fluid catalytic cracking (FCC) in the areas of the petrochemical industry and biomass conversion1.

1 The background description is taken from the MCEC website: http://www.mcec-researchcenter.nl/projects/single-catalyst-particle-diagnostics-droplet-microreactor-platform/
Design and characterization of a microreactor for monodisperse catalytic droplet generation at elevated temperatures and/or pressures


Catalyst particles used in the Fluid Catalytic Cracking (FCC) of crude oil show large variations in activity both between and within particles. This paper reports the results of the fabrication and characterization of a microfluidic droplet microreactor with potential use for single particle diagnostics. The microreactor features a droplet generator, microheaters, micro temperature sensors, and is able to operate at pressures up to 5 bar as of now. This microreactor consists of fluidic channels etched in a silicon wafer and platinum heater and sensor structures embedded in the glass cover. Temperature characterization showed linear behaviour of the sensors with respect to temperature, with a resolution of 0.15 °C, and a sensitivity of 0.0476 Ω°C⁻¹. Furthermore, a PI controller allows control of the heaters within 2.6 °C of the desired temperature. Highly stable and monodisperse oil-in-water droplets are created and heated up to 100 °C at atmospheric pressure, and up to 120 °C at an outlet backing pressure of 5 bar. Preliminary results on the fluorescent detection of the oligomerization reaction of 4-fluorostyrene with zeolite H-ZSM-5 shows the potential of the microreactor chip in investigating the catalytic activity and efficiency of FCC particles.

1. INTRODUCTION

Recent studies show that the particles used in the Fluid Catalytic Cracking (FCC) of crude oil show significant variations in activity both between and within particles [1,2]. These heterogeneous catalysts are under a lot of stress during the cracking process. Metal poisoning and coke formation are examples of contamination that impair the efficacy of a FCC particle [1]. Characterization of the particles is done in large reactors from which only ensemble averages are obtained. So far, the analysis of a single particle is both time consuming and costly [1]. In this paper we present a microfluidic platform dedicated to single particle diagnostics, consisting out of a droplet generator, which can create up to thousands of droplets per second, and a microheater. Inside the droplet, the activity of a single particle can be studied using fluorescence microscopy.

FCC particles are a combination of several materials including clay, zeolite, alumina, and silica. The particle is porous and the pore size decreases towards the centre of the particle. As the oil chain is being cracked when moving into the particle, the smaller components can penetrate deeper into the particle [1]. The cracking of oil takes place at both Lewis and Brønsted acid sites inside the FCC particle. A Brønsted acid site is a solid acid, occurring at places where an aluminum atom is embedded into the silicon lattice, and can attract a proton. Studies have shown that the zeolite inside the FCC particle contains the most solid acid sites, thus being the main active component in the cracking of oil [1–3]. There are several zeolites and from research it is known that its active sites can be studied by either UV-vis spectroscopy [2] or fluorescence microscopy [4]. In both cases an oligomerization reaction of styrene, catalysed by the solid acid sites found in zeolites, is studied. Stavitski et al. 2009 [4], show different styrene additives and the fluorescent intensities that were measured after the reaction of the styrene additives with zeolite H-ZSM-5. The aforementioned reaction takes place between 100 – 200 °C and took about 5 minutes to complete.

In the field of microfluidics the use of microdroplets is common practice. Microdroplets are used in many applications such as chemical microreactors and single particle traps to biological assays of cells and DNA [5–8]. By mixing two immiscible fluids such as oily (nonpolar) and watery (polar) substances, either oil in water (O/W) or water in oil (W/O) droplets are created [5,6,9]. A droplet is the result of the shear forces and interfacial tension between the two fluids, creating a stream of liquid A via joule heating are incorporated on the chip. These platinum heaters are stable up to at least 500 °C [10,11], depending on the adhesion layer that is used. These thin film microheaters have been used a lot in literature [10,11,13–22]. Varying from use in biological assays [16-18,20,21], to reactors or hotplates for single phase purposes [11,13,14,19], and finally to reactions inside droplets on a microfluidic chip [12,17]. In these last two cases this was either done in stationary droplets [17], or with bulky heating systems [12]. The ability to use microfluidic systems at elevated pressures has been demonstrated previously [23,24], where the possibility of both high pressure and high temperature is reported in [23].

Although heterogeneous catalysis has been performed before in droplets on a millifluidic chip [12], this has not been done with an integrated heater section, but in an oven. Other work in microreactors was either not in droplets [11,13,14,19], or if they were, in bulky systems [12], and with stationary droplets [17]. This single catalyst particle diagnostic platform is designed to measure the activity of FCC particles and offers a well-
controlled reaction environment with respect to both volume and temperature; all features integrated into a single microfluidic chip, and without large control systems. The throughput is in theory limited by the optical detection method and the reaction time.

2. DESIGN & SIMULATION

2.1 Design considerations

The chip in Figure 1 (A) shows the design of the microreactor. It has several features, including a droplet generator (C), microreactor (B), and temperature sensor section (D). As the main geometry for creating droplets, the flow focusing junction was chosen for stability reasons. Oil flows in the main channel via inlet I2, and water through the sides via inlet I1 to create droplets of oil in water. The heater section contains three separate heaters. Heater 1 and heater 2 (H1 and H2) can be controlled separately via electrodes E9 and E2. Both these heaters have an interwoven temperature sensor, so they can be monitored and controlled via software. These temperature sensors can be seen in Figure 1 C. A four point measurement, in which a current is steered through electrode E3 and E8, creating a voltage drop over the small resistor structure, is used to measure the resistance of the sensor. The voltage can be measured between electrodes E4 and E5, and electrodes E6 and E7. When the temperature increases, the resistance increases resulting in an increasing voltage across the aforementioned electrodes. The final heater section, H3, is a block of parallel heaters.

These heaters have no dedicated temperature sensor. The parallel heaters are connected to E10; E1 is the ground electrode to which all heaters are connected. When H1 and H2 are at the desired temperature, the power used for heating is calculated and with that the power for H3 can be proportionally estimated via software. The parallel heater section, as well as the meandering structure of the channels, are necessary to give the reaction enough time to occur at elevated temperatures. This standard design has some variations. The channel width varies between 150 – 300 µm, with steps of 50 µm. For some chips a T-junction is used as the droplet generator, and finally the area that is covered by the parallel heater is varied between different chips. The chip as a whole is 15mmx20mmx1mm.

2.2 Simulation

For an estimation of the amount of power that is needed to heat up the fluids in the channel, a COMSOL simulation has been performed. Figure 2 shows the geometry of the device. Because of the symmetry of both heater and channel, only half of the channel is simulated. All surfaces marked with an ‘S’ are the symmetry planes of the simplified model. Further included in the geometry are the silicon substrate (3), the fluid (water) present in the channel (2) and the platinum heating filament (1). The insulating SiO₂ layer on the channel wall has been left out because calculations showed that the transition between silicon and air was the largest thermal barrier i.e. the highest thermal resistance.
In the simulation the heat transfer module, laminar flow model, and Multiphysics for non-isothermal flow, are used. The formula for the stationary heat equation is given below in equation (1) and (2).

\[ pC_p \cdot u \cdot \nabla T + \nabla \cdot q = Q \]  
\[ q = -k \nabla T \]

Where \( p \) is the density in kg m\(^{-3}\), \( C_p \) is the heat capacity at constant pressure in \( \text{Jkg}^{-1}\text{K}^{-1}\), \( T \) is the temperature in K, \( q \) is the heat flux in W m\(^{-2}\), \( Q \) is the volumetric heat flux in W m\(^{-3}\), and \( u \) is the velocity vector in \( \text{ms}^{-1}\). Note that bold variables/parameters \( u \) and \( q \) are vectors and other variables/parameters are scalars or mathematical operators.

For the laminar flow domain, a parabolic flow profile is present at the inlet. The formula used for the determination of the laminar flow profile is given in equation (3) taken from [25].

\[ v_z = \frac{9}{4HW} \left( 1 - 4 \left( \frac{y_y + \Delta y}{H} \right)^2 \right) \left( 1 - 4 \left( \frac{z_z + \Delta z}{W} \right)^2 \right) \]

Where \( v_z \) is the velocity in the z-direction in \( \text{ms}^{-1}\), \( H \) is the height of the channel in m, \( W \) is the width of the channel in m, \( y_y \) and \( z_z \) are at the origin of the channel, which indicated with an ‘O’ in Figure 2, \( Q_f \) is the flow rate in m\(^3\)s\(^{-1}\). The walls of the channel were given no slip condition, meaning that \( v = 0 \) at the walls. Boundary conditions used in the simulation are listed below and clarified in Figure 2.

Inlet velocity profile (A): Equation (3) was given as a formula for the velocity profile of the flow.

Heat flux condition (B1 and B2): The heat flux is the outflow of heat normal to the surface area. The convective heat flux is given by: \( q_o = h(T_{ext} - T) \), where \( h \) is the heat transfer coefficient in W m\(^{-2}\)K\(^{-1}\), \( T_{ext} \) and \( T \) are the temperatures outside and inside the device in K. Calculations gave an estimation for the heat loss as if the simulated geometry were the size of the design, resulting in a heat transfer coefficient of 953 W m\(^{-2}\)K\(^{-1}\) for surfaces marked by B1, and a smaller heat transfer coefficient for surfaces in normal contact with air, B2, with a heat transfer coefficient of 10 W m\(^{-2}\)K\(^{-1}\).

Heat source (C): The platinum element is modelled as a heat source with an empirically determined power of 300 mW.

Thermally insulating (D): The symmetry plane and the sides of the heater were made thermally insulating.

No viscous stress (E): The symmetry surface of the channel is given a no viscous stress condition, to allow the fluid to have a velocity at this surface, therefore create half of a parabolic flow profile.  

Material properties and parameters used in the simulation are listed in Table 1. The simulation result shows a cross-section of the channel and the corresponding temperature profile inside the channel, as shown in Figure 3. Because the temperature is uniform (Uniformity is shown in Supplementary Information SI.1) along the length of the channel, this can be at any point on the z-axis. This temperature is in the range of the temperature needed for the reaction. With this result the power per unit area for the platinum heat source in the simulation was related to the total contact area between the heaters and the channel in the design. This leads to an estimated power of 1.13 W.

Table 1: Parameters for the different materials used in the calculation of the heat transfer coefficient of the microreactor

<table>
<thead>
<tr>
<th></th>
<th>Thermal conductivity (W/m(^{-2})K(^{-1}))</th>
<th>Density (kg/m(^{3}))</th>
<th>Heat transfer coefficient (W/m(^{2})K(^{-1}))</th>
<th>Thermal capacity (J/kg.K(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>0.6</td>
<td>1</td>
<td>N.A.</td>
<td>4185.5</td>
</tr>
<tr>
<td>Si</td>
<td>130</td>
<td>2329</td>
<td>N.A.</td>
<td>700</td>
</tr>
<tr>
<td>Platinum</td>
<td>71.6</td>
<td>21450</td>
<td>N.A.</td>
<td>133</td>
</tr>
<tr>
<td>Air</td>
<td>N.A.</td>
<td>N.A.</td>
<td>10</td>
<td>N.A.</td>
</tr>
</tbody>
</table>

\(^{2}\) In Supplementary Information (SI.1) more about the exact shape of this “half” parabolic flow profile is given.
3. EXPERIMENTAL

3.1 Fabrication

The chips were fabricated in cleanroom of the MESA+ NanoLab at the University of Twente. Figure 4 shows an overview of the process steps that were done to fabricate the chip. Supplementary Information (SI.2) provides more information about the masks that were used during the processing. The chip is a stack of a silicon and a glass substrate bonded together. A three mask process is used to develop the desired features in/on both substrates, as shown in Figure 4. Using photolithography with mask 1, the pattern for the platinum structures is created on a glass substrate. With BHF as a wet etchant the pattern is etched 200 nm deep into the glass substrate. This process is directly followed by the deposition of a 10 nm thick tantalum adhesion layer and a 190 nm thick platinum layer, causing the heater to be embedded into the glass substrate. After this the complete glass substrate is covered with 1 μm PECVD SiO2 and mask 3 is used to remove this SiO2 layer from the contact electrodes and at the fluidic accesses. Mask 2 is then used to create the channel pattern on the silicon substrate. The channels are made 150 μm deep using DRIE etching. With mask 3 the pattern for the contact holes and fluidic accesses was made on the backside of the silicon substrate; this time DRIE etching is used to etch all the way through the silicon. This ensures the accessibility of the electrodes and channels when the substrates are bonded together. Before that final step the silicon substrate is first put into the oven for dry oxidation of Si. This creates the 200 nm thin insulating SiO2 film on the walls of the channel. Post to completion of all process steps, the silicon and glass substrates are anodically bonded, and the individual chips released by dicing.

3.2 Temperature sensor characterization

Characterization of the temperature sensors is done by mounting the chip on a Printed Circuit Board (PCB) and wirebonding the electrodes to the PCB, so the chip can be addressed via external connectors. The chip is fully immersed in a beaker of oil standing on a hotplate, type IKA RET. A thermocouple thermometer, connected with the hotplate, is used as a reference thermometer and measures the temperature of the oil. A magnetic stirring bead is added to increase the uniformity of the temperature in the oil. The hotplate is heated from 30 °C to 150 °C and back, to rule out any hysteresis effects. Meanwhile the resistance of the temperature sensor on the microreactor is measured. A signal from the sensor is measured by steering a current through it, using a LM317TG voltage regulator as current source. The voltage occurring across the resistor is amplified using a AD620ANZ instrumentation amplifier. The output signal is recorded by a NI myRIO connected with Labview software on the computer. Supplementary Information (SI.3) provides more information about read-out electronics.

3.3 Chipholder and control of the heaters

For control of the heaters, the chip is placed into a Delrin chipholder, chosen for its low thermal conductivity. This chipholder consists of a bottom and top part. For control of the heaters a PI controller is made in Labview and executed on the NI myRIO. The PI controls the duty cycle of a 1000 kHz square wave put onto the gate of a NMOS transistor FDN5630. The NMOS acts as a switch between a 48V power source and the heaters. By varying the duty cycle the power to the heaters can be controlled. The temperature sensors in the microreactor chip provide the feedback temperature for the control loop. Supplementary Information (SI.3) provides more information about the control.

3.4 Droplet creation

Droplets are created by connecting a Nemesys syringe pump, with Hamilton syringes of 500 μL (oil) and 1000 μL (water), Fused silica tubing (Polyimico Technologies, ID = 100 μm, OD = 360 μm), to the oil and water inlets of the microreactor. The pump is controlled with Nemesys software. For the dispersed phase FC-40 oil is used and for the continuous phase MilliQ demiwater. A CCD high speed camera and FPV software, in combination with a Leica DMI 5000 M microscope is used to capture movies and images from the droplets whilst created. Experiments at high pressure can be done by adding a backpressure regulator, P786 from idex-hs, with a backing pressure of 5 bar.
3.5 High temperature reactions inside droplets

For proof of principle testing, an oligomerization reaction with zeolite H-ZSM-5 powder and 4-fluorostyrene, suspended in hexadecane (all from Sigma Aldrich), is done inside the microreactor chip. This reaction, previously done by Aramburo et al 2012 [3], is illustrated in Scheme 1. Aforementioned reaction does not take place at room temperature and starts up slowly at 80 °C [4]. The reaction products, shown in Scheme 1, are a linear dimeric carbocation (D) and a cyclic dimeric species (E), having an absorption band at 520 nm and 565 nm respectively [3]. Fluorescence images are made of the inside of the channels of the microreactor at room temperature and at 140 °C. The excitation wavelength of the laser that is used is 561 nm and the emission of the sample is 605 nm. Images are captured with a Nikon Eclipse confocal fluorescence microscope.

For proof of principle testing, an oligomerization reaction with zeolite H-ZSM-5 powder and 4-fluorostyrene, suspended in hexadecane (all from Sigma Aldrich), is done inside the microreactor chip. This reaction, previously done by Aramburo et al 2012 [3], is illustrated in Scheme 1. Aforementioned reaction does not take place at room temperature and starts up slowly at 80 °C [4]. The reaction products, shown in Scheme 1, are a linear dimeric carbocation (D) and a cyclic dimeric species (E), having an absorption band at 520 nm and 565 nm respectively [3]. Fluorescence images are made of the inside of the channels of the microreactor at room temperature and at 140 °C. The excitation wavelength of the laser that is used is 561 nm and the emission of the sample is 605 nm. Images are captured with a Nikon Eclipse confocal fluorescence microscope.

4. RESULTS

4.1 Temperature sensor characterization

Successful fabrication resulted in the chip shown in Figure 6. Showing all features like, the droplet generator, heaters (H1, H2, and H3), temperature sensors, inlets (oil and water), outlet, and the optical window, as mentioned in section 2.1 regarding the design. Created channels are 150 μm deep. Temperature characterization is performed using the oil immersion method as described in the experimental section. The results are shown, for the sensor (S1) at H1 only, in Figure 7. The graph for the other sensor (S2) can be found in Supplementary Information (SI.4). The temperature characteristic of the sensors is highly linear, given the R² of 0.99899 for S1 and an R² of 0.9989 for S2. The sensitivity for both sensors is 0.0476 Ω°C⁻¹, and the offsets are 18.311 Ω and 18.294 Ω for S1 and S2 respectively. Because of the uniformity, this characteristic is used for all the sensor structures made on the same wafer, since they were made in the same process. From this characteristic also the resistivity and temperature coefficient of resistance (TCR) for the platinum layer is calculated, being 1.6667e⁻⁷ Ω m and 0.0025 °C⁻¹ respectively.

The resolution of the temperature sensors is 0.15 °C, determined by the 12 bit ADC and gain of the electric circuit amplifying the voltage across S1 and S2. More information regarding the read-out circuit can be found in Supplementary Information (SI.3).

4.2.1 Control of the heaters H1 and H2

Testing the control of the heater is done by varying the setpoint of the PI control described in section 3.3. The setpoint of the control loop is varied between 23 °C and 120 °C; during these experiments droplets were created at the same time inside the microreactor chip. It can clearly be seen that when the setpoint is increased from 50 °C to 75 °C, the duty cycle increases immediately, resulting in an increased power dissipation, and therefore increased temperature of the heater. The step response time (time needed to reach the setpoint) is approximately 1.5 seconds after which the temperature oscillates around the setpoint. There is a standard deviation of 2.6 °C around the setpoint and calculations shows that 530 mW is needed to reach 50 °C. More information about the control measurements regarding H1 and H2, and the calculated values above, can be found in Supplementary Information (SI.4) .
4.2.2 Use of the parallel heaters

The parallel heaters (H3) can be manually controlled via the Labview software. They are connected to a different NMOS than H1 and H2. The parallel heaters generate enough heat to be measured by S1 and S2. By carefully adjusting the duty cycle of H3, it can be optimally tuned for assisting H1 and H2. More information about the control measurements regarding H3 can be found in Supplementary Information (SI.4).

4.3 Droplets at different temperatures and pressure

Droplets were created using the setup described in section 3.4. Several tests were done with droplets being created in various conditions, as shown in Figure 8, where A) the heaters are switched off, B) the temperature is kept at 50 °C and C) 75 °C, D) the temperature is above the boiling point of water (120 °C), and finally E) the temperature is above the boiling point of water (120 °C), but the system is under an outlet pressure of 5 bar approximately. For all measurements the flow rates of the water and oil phase are 15 µL/min and 3 µL/min respectively, and images were taken by the high-speed camera with a framerate of 125 fps. The width of the channel is these measurements was 250 µm. Figure 8 A) shows the image of droplets created at room temperature. The created droplets are highly monodisperse, as shown in Figure 8 B) and C), where droplets at 50 °C and at 75 °C are depicted. The volume of the droplet is approximately 47 nL and does not change with temperature. The volume was determined by using height and width of the channel and the length of the heater filament covered by the droplet. A measurement with a different chip at different flowrates is shown in Supplementary Information (SI.5) to provide more data on monodispersity and droplet volume. When the temperature is increased to 100 °C, small gas bubbles start to appear in the channel. The bubbles find their origin under the heater and when they encounter an oil droplet they show affinity towards the oil phase. Inside the oil bubble the small bubbles seem to follow the path of the heater. Figure 9 illustrates the appearance of gas bubbles, their accumulation in the oil droplet, and their behaviour in following the heater trace. At 120 °C large gas bubbles are formed and the droplets start to fall apart, showing dewetting phenomenon at the channel ceiling surface. A collapsed droplet, with large gas bubbles in the droplet, is shown in Figure 8 D). When the backpressure regulator is added, the droplets are still intact at 120 °C. This is shown in Figure 8 E). The monodispersity is warranted when working above atmospheric pressure at the outlet.

4.4 Reaction in single phase flow

In order to observe the influence of temperature on the reaction, first a control measurement is done. For this control measurement, the H-ZSM-5 with 4-fluorostyrene and hexadecane mixture is flushed through the chip with the heaters off. A flow rate of 3 µL/min is used. The fluorescence image shown in Figure 10 A) is taken at a spot in the channel, at room temperature. The heaters are then set at a temperature of 140 °C and a fluorescence image is taken from the same part of the channel. These figures show that there is a small change in fluorescence signal for this particular area when the heaters are switched on, with respect to when they are switched off.
Upon completion of the measurement other areas of the chip were inspected and a large agglomeration of particles near the inlet was observed. Apparently, the zeolite particles attached to the wall, as shown in Figure 10 B). These fluorescent parts around the inlet could not be flushed out of the channel, even with high flow rates up to 120 µL/min.

5. Conclusion and outlook

Successful creation of droplets, as well as heating the droplet under high pressure has been achieved with the droplet microreactor. Fabrication of the microreactor has been achieved with a three mask process. Preliminary results show proof of principle, in a one phase flow, by the oligomerization reaction of 4-fluorostyrene with zeolite H-ZSM-5 at 140 °C, whereas the reaction does not occur at room temperature. Generated droplets are highly monodisperse, creating well defined and uniform reaction environments. The temperature of the heater elements can be controlled with a standard deviation of approximately 2.6 °C from the setpoint. Measurement of the temperature can be done with a resolution of 0.15 °C. The appearance of gas bubbles inside stable oil droplets around 100 °C gives the opportunity to study reactions with gas on the chip in a three phase system.

As of now, the proof of principle reaction has been done in a one phase flow. In order to get more elaborate and conclusive proof about the ability to do controlled reactions on the chip, the reaction needs to be done in an actual droplet. This can give more insight to the reaction rates when the fluorescent intensity is measured as the droplet travels along the channel. Furthermore, instead of zeolite powder, the real FCC particles should be tested. To do this, the particles must be captured in droplets first. This might cause problems, because it is known that FCC particles sink quickly, and thus do not stay in suspension. Upon achievement of FCC particle encapsulation their activity and behaviour can be studied on chip. Finally, the temperature inside the channel needs to be calibrated, since the temperature read-out from the platinum sensors solely contains information about the temperature on the surface of the channel, on only two places. In collaboration with Utrecht University, luminescent nanoparticles can be used to map the temperature inside channels [26], as well as the temperature distribution over the chip as a whole.
Acknowledgements
This work was supported by the Netherlands Center for Multiscale Catalytic Energy Conversion (MCEC), an NWO Gravitation programme funded by the Ministry of Education, Culture and Science of the government of the Netherlands. Further gratitude is reserved for S. Dekker, H. de Boer, C. Brunink for helping with fabrication of both chip and chipholders. M. Welleweerd is thanked for his expertise in Solidworks and Photoshop.

Notes and references


SUPPLEMENTARY INFORMATION

SI.1 Clarifications on calculations and choices made in the simulation process

SI1.1 Simulation geometry
For an estimation of the amount of power that is needed to heat up the fluids in the channel, a COMSOL simulation has been performed. Figure 1.1 shows the geometry of the device. Because of the symmetry of both heater and channel, only half of the channel is simulated. Further included in the geometry are the silicon wafer (3), the fluid (water) that is present in the channel (2) and the platinum heater element (1). This is a simplified representation of the design, whereas in the actual design the wall of the channel would contain a second phase for the droplets, a thin insulating layer of 200 nm silicon dioxide, more bulk silicon, and a glass layer on top. All the simplifications mentioned above are done to reduce the simulation time.

SI1.2 Heat loss estimation
The heat transfer coefficient, \( h \) in Wm\(^{-2}\)K\(^{-1}\), that represents the amount of silicon and glass that is exposed to air is calculated and used to give a value for the outflux of heat per channel wall.

\[
Q = UA(T_i - T_0)
\]  

In which \( U \) is the overall heat transfer coefficient in Wm\(^{-2}\)K\(^{-1}\), \( A \) is the surface area in m\(^2\), \( T_i \) and \( T_0 \) are the temperatures in K. \( U \) can be further expressed as in equation (2) \cite{1}, where it is the summation of all individual thermal resistances of the different blocks.

\[
\frac{1}{U} = \frac{1}{k_{\text{water}}} + \frac{L_{\text{SiO}_2}}{k_{\text{SiO}_2}} + \frac{L_{\text{Si}}}{k_{\text{Si}}} + \frac{1}{h_{\text{air}}}
\]  

In which \( k \) (Wm\(^{-1}\)K\(^{-1}\)) and \( L \) (m) are the thermal conductivity and length of each individual block, and \( h_0 \) Wm\(^{-2}\)K\(^{-1}\) is the heat transfer coefficient of air, which is 10 Wm\(^{-2}\)K\(^{-1}\). The calculation shows that the overall heat transfer coefficient is mostly determined by the transition from silicon to air, since it has the highest thermal resistance, limiting the heat flow the most.
In this 2D model only the heat loss through the side of the channel is calculated, so for the total surface area, also the top and bottom are taken into account. The eventual chip will be 15mmx20 mmx1mm, and because of the symmetry, only half of its surface area is used in the model to calculate the heat losses. The total surface area that is in contact with the air for said chip is $3 \times 10^{-4}$ m$^2$. In steady state the heat flow, as well as the internal and external temperature, is constant. In order for the small scale COMSOL model to reach the same steady state level, the heat transfer coefficient times the area through which heat is lost, should be constant as well. With the calculated heat flux coefficient for the aforementioned area, the small scale heat flux coefficient can be calculated with the dimensions of the geometry of the model from Figure 1.1. Subsequently resulting in an equivalent model area of $3.15 \times 10^{-6}$ m$^2$. For the walls in direct contact with air, as seen in Figure 1.1, a heat flux coefficient of $10 \text{ Wm}^{-2}\text{ K}^{-1}$ is used. The heat loss coefficient for the walls representing a larger area are then:

$$U_{\text{model}} = \frac{3 \times 10^{-4} \times 10}{3.15 \times 10^{-6}} = 953 \frac{\text{W}}{\text{m}^2\text{K}}$$

The model is solved for a stationary study with the heat transfer module, laminar flow model, and Multiphysics for non-isothermal flow.

The resulting parabolic flow profile that was obtained with equation (3), and is shown in Figure 1.3. Here it can be seen that the “half” parabolic flow profile has its maximum at the symmetry line, indicated with an ‘S’ in Figure 1.3.

$$v_z = \frac{9}{4} \frac{Q_f}{H W} \left( 1 - 4 \left( \frac{y + \Delta y}{H} \right)^2 \right) \left( 1 - 4 \left( \frac{x + \Delta x}{W} \right)^2 \right) \quad (3)$$

Where $v_z$ is the velocity in the $z$-direction in m s$^{-1}$, $H$ is the height of the channel in m, $W$ is the width of the channel in m, $y_0$ and $z_0$ are at the origin of the channel, which indicated with an ‘O’ in Figure 1.1, $Q_f$ is the flow rate in m$^3$s$^{-1}$. The walls of the channel were given no slip condition, meaning that $v = 0$ at the walls. Boundary conditions are clarified in Figure 1.1. The temperature distribution through the whole geometry is shown in Figure 1.4. Furthermore, in Figure 1.5 the temperature gradient from top to bottom of the channel can be seen. The line is also taken at the symmetry line ‘S’.

Because the sides of the heating element are made thermally insulating and the heat loss through the top of the heater is small compared to the heat exchange between the channel and the heater, the power per unit area (the contact area between the heater and the channel) can be calculated with the simulation results. In the simulation this means that there is $6.67 \text{e}5 \text{ W/m}^2$. Using the contact area between the heater and the channel from the design, approximately $1.13 \text{ W}$ is needed to heat the channel up to 155 °C, according to the simulation.
SI.2 Masks used in fabrication process

The masks used in the process flow are shown below in Figure 2.1, Figure 2.2, and Figure 2.3 and were made in Clewin. The first mask (Figure 2.1) is used for creating the thin film structures, like the heaters and sensors in the glass substrate. The second mask (Figure 2.2) is used to etch channel structures in the silicon substrate, and finally the third mask (Figure 2.3) is used to create electronic and fluidic accesses in the silicon substrate. These masks are used in the process flow listed in Supplementary Information (SI.6). In the comment section of the process flow the mask number that is used for each lithography step is listed.

Figure 2.1: Mask 1 used for patterning of thin film structures on the glass substrate

Figure 2.2: Mask 2, used for patterning of the fluidic channels in the silicon substrate

Figure 2.3: Mask 3, used for patterning of the electrical and fluidic accesses.
SI.3 Electrical circuits used for measurement and control

Schematic of the temperature sensor read-out circuit Figure 3.1 and heater control circuit Figure 3.2 will be explained. In the sensor read-out structure, the LM317TG is used as a current source. The formula for the output current is given by equation (4).

\[ I_{\text{out}} = \frac{1.25}{R_1} \]  

(4)

\( I_{\text{out}} \) is chosen to be 2 mA as to not heat up the structure by this bias current. This makes \( R_1 \) 625 Ω. The current through the sensor causes a voltage drop across the resistors. This voltage is amplified using a AD620ANZ instrumentation amplifier. The formula used in calculating the gain of this amplifier is shown in equation (5).

\[ \text{Gain} = \frac{49.4}{R_{\text{Gain}}} + 1 \]  

(5)

The gain is chosen in such a way that the voltage across at the output of the amplifier would be 5V when the resistor has a temperature of 250 °C. This was done get enough gain in the desired temperature range, but to have some margin with the upper limit of the 12 bit ADC of the myRio. These considerations result in a gain of 82, making \( R_{\text{gain}} \) 610 Ω. The 12 bit ADC and the choices for the gain of the instrumentation amplifier result in a resolution of 0.15 °C for the whole sensor circuit.

For the heater actuation a PI control is used, executed by the myRio board. The circuit in Figure 3.2 shows how control is done. The gate of the NMOS is connected to the PWM output port of the myRio. Depending on the temperature setpoint, controlled in the software, the myRio controls the duty cycle of a 1 kHz square wave coming out of the PWM port. A duty cycle value of 1 means a DC voltage of 3.3 V, and a duty cycle of 0 means 0 V on the gate of the NMOS. Heaters H1 and H2 are connected to the same NMOS, because they are so close together that it is not possible to set them both at a completely different temperature, without influencing each other’s read-out.

Figure 3.1: Electrical read-out circuit used in amplification and measurement of the voltage across the temperature sensor structures S1 and S2.

Figure 3.2: Electrical circuit used in the control of the power in the heater H1, H2, and H3.
SI.4 Temperature sensor characterization of S2, and control measurements of heaters H1, H2 and H3

SI.4.1 Temperature sensor (S2) characterization

The temperature characteristic of S2 is given in this Supplementary information. The characterization is done in the same experiment as for S1, with the oil immersion method. Figure 4.1 shows the graph that was obtained for R2. It has a sensitivity of 0.0476 °C⁻¹, which is the same as for S1, and an offset of 18.294 °C. The measure of linearity, R², is 0.9989.

Figure 4.1: Temperature characteristic of S2

SI.4.2 Control of H1 and H2

Figure 4.2 and Figure 4.3 show the temperature readout of both sensors (S1 and S2) and the corresponding duty cycle applied to the gate of the NMOS, for a transient response from 50 °C to 75 °C.

The mean temperature value of the part starting at 18.6 seconds and ending at 39 seconds in Figure 4.2 is 76.03 °C with a standard deviation of 2.56 °C. The same interval for Figure 4.3 gives a mean of 76.51 °C and a standard deviation of 2.60 °C. The power used in heating the chip is calculated with the resistance of the heater, the duty cycle, and the voltage across the resistor. The calculation shows that 530 mW is needed to reach 50 °C.

Figure 4.2: Step response of the control loop showing the temperature at H2 and the duty cycle controlling the power in H2. After 18 seconds the setpoint was changed from 50 °C to 75 °C.

Figure 4.3: Step response of the control loop showing the temperature at H1 and the duty cycle controlling the power in H1. After 18 seconds the setpoint was changed from 50 °C to 75 °C.
SI.4.3 Control of H3

The parallel heaters (H3) can be controlled via the Labview software. They are connected to a different NMOS than H1 and H2. In the software the duty cycle can be adjusted. Figure 4.4 illustrates the influence of the parallel heaters on the control loop.

During this experiment the duty cycle of H3 is gradually increased. In the beginning the temperature is mainly maintained by H1 and H2, but when the duty cycle of H3 is increased, it is visible that the duty cycle of H1 and H2 is going down. This is starting around t1. At t2 the duty cycle for H1 and H2 is 0, but the temperature increases. The increase comes from the heat generated solely by H3. By decreasing the duty cycle of H3 again, the temperature can be made constant around the setpoint, as shown at t3. The ideal duty cycle for H3 can be manually determined by looking at the behaviour of the system.

Figure 4.4: Temperature of H2 dependent on activation of

A) The duty cycle controlling H1 and H2 and B) The duty cycle controlling H3. At t1 the duty cycle of H1 and H2 starts to decrease and at t2 it is 0. From t2 the temperature at H2 increases as a result of the heat produced by H3. Finally at t3 the duty cycle of H3 has been adjusted to maintain the temperature at the pre-set level of 75 °C.
SI.5 Droplet monodispersity

Images of droplets at different flow rates were taken and the volumes of the droplets are compared within and between experiments. The ratio of flow rates between the water and oil phase was kept constant during the experiments, being water:oil 3:1. Flow rates of 9 vs 3 μL/min, 45 vs 15 μL/min, and 90 vs 30 μL/min, were tested. The results are shown in Figure 5.1. It can be seen that the volume of the droplets decreased when the flow rate goes up. The volume was calculated with the height width of the channel being 150 μm and 250 μm respectively. The length was calculated by looking at how many segments of the heater the droplet spanned. Volume of the droplets was 21 pL, 14 pL, and 11 pL. Within the measurements the monodispersity of the droplets was high, as shown in Figure 5.1.

![Figure 5.1: Droplets created at different flow rates for the water and oil phase. Flow rate ratio is kept equal, being water:oil 3:1](image)
### Process flow

**Name of process flow:** Droplet microreactor  
**Platform:** Fluidics  
**Creation date:** 2016-06-23  
**Personal information**  
**User name:** Vollenbroek, Jeroen (BIOS)  
**Email address:** j.c.vollenbroek@student.utwente.nl  
**Company/Chair:** Masterstudenten  
**Function:** Other  
**Project:** MCEC Droplet platform  
**Name of supervisor:** Mathieu Odijk  

**Process planning**  
**Process start:** 2016-04-04  
**Process end:** 2016-04-18  
**Status**  
**Name of advisor:** Bruinink, Christiaan (MESA)  
**Last revision:** 2016-06-23  

**ILP: In-line Processing** | **MFP: Metal-free Processing** | **UCP: Ultra Clean Processing** | **Removal of Residues**
---|---|---|---

**Step Level Process/Basic flow**  
| 1 | **Substrate Silicon** (#subs101) | NL-CLR-Wafer Storage Cupboard  
Orientation: <100>  
Diameter: 100mm  
Thickness: 525µm +/- 25µm  
Polished: Single side (OSP)  
Resistivity: 5-10Ωcm  
Type: p/boron | **User comments** | **litho1801: Lithography of Olin Oir 907-17 (positive resist - ILP)** |
Dehydration bake

Dehydration bake on hotplate
• Temperature: 120°C
• Time: 5min

After the dehydration bake, perform the wafer priming with minimum delay!

Priming HMDS

Coating: Primus Spinner
• HexaMethylDiSilazane (HMDS)
• Spin program: 4000 (4000rpm, 30sec)

Coating of Olin OiR 907-17

Coating: Primus spinner
• Olin OiR 907-17
• Spin program: 4000 (4000rpm, 30sec)

2000 rpm instead of 4000 rpm

Prebake of Olin OiR 907-17

Prebake: Hotplate
• Temperature: 95°C
• Time: 90s

Alignment & exposure of Olin OiR 907-17

Electronic Vision Group EV620 Mask Aligner
• Hg-lamp: 12 mW/cm²
• Exposure time: 4sec

After exposure bake of Olin OiR resists

After exposure bake: Hotplate
• Temperature: 120°C
• Time: 60s

Development of Olin OiR resists

Development: OPD4262
• Beaker 1: 30sec
• Beaker 2: 15-30sec

Quick Dump Rinse (QDR)

Recipe 1 Quick dump rinsing (QDR)
Recipe 2 Cascade rinsing for fragile wafers
Rinse until message 'End of rinsing process' is shown on the touchscreen of the QDR, else repeat the rinsing process.

Substrate drying

Single substrate drying:
1. Use the single-wafer spinner
   • Settings: 2500 rpm, 60 sec (including 45 sec nitrogen purge)
2. Use the nitrogen gun (fragile wafers or small samples)
Postbake of Olin OiR resists
(#litho008)

Postbake: Hotplate
- Temperature: 120°C
- Time: 10min

Inspection by optical microscope
(#metro101)

- NL-CLR- Nikon Microscope
- dedicated microscope for lithography inspection

DRIE of silicon STD high rate
(#etch212)

- NL-CLR-SPTS Pegasus
- Bosch High rate for micro features
- Platen temp: -19°C - He pres: 20Torr

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Etch</th>
<th>Deposition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas</td>
<td>SF6</td>
<td>C4F8</td>
</tr>
<tr>
<td>Flow [sccm]</td>
<td>800</td>
<td>400</td>
</tr>
<tr>
<td>Boost Flow [sccm - sec]</td>
<td>350 - 1.5</td>
<td>-</td>
</tr>
<tr>
<td>Time [sec]</td>
<td>7</td>
<td>2</td>
</tr>
<tr>
<td>APC [%]</td>
<td>8</td>
<td>8</td>
</tr>
<tr>
<td>ICP [Watt]</td>
<td>3000</td>
<td>3000</td>
</tr>
<tr>
<td>CCP [Watt]</td>
<td>40 (RF)</td>
<td></td>
</tr>
<tr>
<td>Boost CCP [Watt - sec]</td>
<td>300 - 2.5</td>
<td>-</td>
</tr>
</tbody>
</table>

Etch rate: Si: 20-30 um/min

Chamber/chuck clean
(#etch219)

- NL-CLR-SPTS Pegasus
- Name: TDSec clean

- Parameters:
  - Flow: 200 sccm O2
  - Pressure: 5 mTorr
  - ICP: 2500W
  - CCP: 20W (RF)
- 15 minutes after use
- After cleaning the substrate holder temp will be set tot 20°C

The 3 min version will not change the temperature

Removal of Fluorocarbon
(#residue104)

- NL-CLR-TePla 360
- Purpose: removal of Fluorocarbon in O₂/CF₄ Plasma after BOSCH etching, including any resists present on the substrate.

- WARNING: this recipe also attacks silicon and nitride coatings for several nanometers!
Recipe 071

1- Removal of Resists
O₂ flow: 500sccm
Pressure: 0.8mbar (35% valve)
Power: 600Watt
Time: 20 min

2- Removal of Fluorocarbon
O₂ flow: 475sccm
CF₄ flow: 25sccm
Pressure: 0.8mbar (35% valve)
Power: 800Watt
Time: 1min

3- Removal of residual Fluorocarbon
O₂ flow: 500sccm
Pressure: 0.8mbar (35% valve)
Power: 800Watt
Time: 1min

---

litho1802: Lithography of Olin Oir 908-35 (positive resist - ILP)

16 ILP Dehydration bake
(#litho001) NL-CLR-WB21/22
Dehydration bake on hotplate
• Temperature: 120°C
• Time: 5 min

After the dehydration bake, perform the wafer priming with minimum delay!

17 ILP Priming HMDS
(liquid)
(#litho600) NL-CLR-WB21/22
Coating: Primus Spinner
• HexaMethylDisilazane (HMDS)
• Spin program: 4000 (4000rpm, 30sec)

18 ILP Coating of Olin OiR
908-35
(#litho102) NL-CLR- WB21
Coating: Primus coater
• Olin OiR 908-35
• Spin program: 4000 (4000rpm, 30sec)

Use 2000 rpm instead of 4000 rpm

19 ILP Prebake of Olin OiR
908-35
(#litho004) NL-CLR-WB21
Prebake: Hotplate
• Temperature: 95°C
• Time: 120s

20 ILP Alignment & exposure of Olin OiR
908-35
(#litho302) NL-CLR- EV620
• Electronic Vision Group EV620 Mask Aligner
• Hg lamp: 12 mW/cm²
• Exposure time: 9 sec

MASK 3
After exposure bake of Olin OiR resists (#litho005)

- NL-CLR-WB21
- **After exposure bake:** Hotplate
  - **Temperature:** 120°C
  - **Time:** 60s

Development of Olin OiR resists (#litho200)

- NL-CLR-WB21
- **Development:** OPD4262
  - **Beaker 1:** 30sec
  - **Beaker 2:** 15-30sec

Quick Dump Rinse (QDR) (#rinse119)

- NL-CLR-Wetbenches
- **Purpose:** removal of traces of chemical agents.
  
  - **Recipe 1 Quick dump rinsing (QDR)**
  - **Recipe 2 Cascade rinsing for fragile wafers**
  - Rinse until message ‘End of rinsing process’ is shown on the touchscreen of the QDR, else repeat the rinsing process.

Substrate drying (#dry120)

- NL-CLR-WB
- **Single substrate drying:**
  1. Use the single-wafer spinner
     - **Settings:** 2500 rpm, 60 sec (including 45 sec nitrogen purge)
  2. Use the nitrogen gun (fragile wafers or small samples)

Postbake of Olin OiR resists (#litho008)

- NL-CLR-WB21
- **Postbake:** Hotplate
  - **Temperature:** 120°C
  - **Time:** 10min

Inspection by optical microscope (#metro101)

- NL-CLR- Nikon Microscope
- • dedicated microscope for lithography inspection

DRIE of Si A pulsed C4F8 at -40°C (#etch175)

- NL-CLR-Adixen SE
  - **Application:** trenches, wafer through using thick photoresist (908-35)
  - Use: C4F8 flow and CCP for tuning process.
  - **SH temp:** -40°C - Pos: 110mm - He pres: 10mbar
  - **Use foil on top of wafer to prevent He leak.**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Etch</th>
<th>Deposition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas</td>
<td>SF₆</td>
<td>C₄F₈</td>
</tr>
<tr>
<td>Flow (sccm)</td>
<td><strong>500</strong></td>
<td><strong>175</strong></td>
</tr>
<tr>
<td>Time (sec)</td>
<td>4</td>
<td>0.5</td>
</tr>
<tr>
<td>Priority</td>
<td>2</td>
<td>1</td>
</tr>
<tr>
<td>APC %</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>ICP (Watt)</td>
<td>2500</td>
<td>2500</td>
</tr>
<tr>
<td>CCP (Watt)</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Pulsed (msec)</td>
<td>20on/80off</td>
<td>20on/80off</td>
</tr>
</tbody>
</table>
Removal of Fluorocarbon
(#residue103)

Purpose: removal of Fluorocarbon in O2/CF4 Plasma after BOSCH etching, including any resists present on the substrate.

**WARNING**: this recipe also attacks silicon and nitride coatings for several nanometers!

1- **Preheating**
   - Ar flow: 600sccm
   - Pressure: 0.6mbar
   - Power: 1000Watt
   - Time: 10min

2- **Removal of Resists**
   - O2 flow: 250sccm
   - Pressure: 0.5mbar (35% valve)
   - Power: 800Watt
   - Time: depending on recipe*

3- **Removal of Fluorocarbon**
   - O2 flow: 237sccm
   - CF4 flow: 13sccm
   - Pressure: 0.5mbar (35% valve)
   - Power: 800Watt
   - Time: 1min

4- **Removal of residual Fluorocarbon**
   - O2 flow: 250sccm
   - Pressure: 0.8mbar (30% valve)
   - Power: 800Watt
   - Time: 1min

* Select one of the following recipes to remove the fluorocarbon and strip resists, depending on the thickness of the resist, treatment of the resist and the number of wafers.

**Recipe 035**: time = 10 min
**Recipe 037**: time = 20 min

film1685: Dry oxidation of silicon at 1100 C (H1)

NL-CLR-WB14
Purpose: removal of organic traces.
- Beaker 1: 99% HNO3
- Time = 5 min
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>30</td>
<td></td>
<td></td>
<td>• Beaker 2: 99% HNO₃</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Time = 5 min</td>
</tr>
<tr>
<td>31</td>
<td></td>
<td>Quick Dump Rinse (QDR) (rinse120)</td>
<td>Purpose: removal of traces of chemical agents.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Recipe 1 Quick dump rinsing (QDR)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Recipe 2 Cascade rinsing for fragile wafers</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Rinse until message ‘End of rinsing process’ is shown on the touchscreen of the QDR, else repeat the rinsing process.</td>
</tr>
<tr>
<td>32</td>
<td></td>
<td>Cleaning in 69% HNO₃ at 95 °C (clean003)</td>
<td>Purpose: removal of metallic traces.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Beaker 3A or 3B: 69% HNO₃</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Temperature= 95 °C</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Time = 10 min</td>
</tr>
<tr>
<td>33</td>
<td></td>
<td>Quick Dump Rinse (QDR) (rinse120)</td>
<td>Purpose: removal of traces of chemical agents.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Recipe 1 Quick dump rinsing (QDR)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Recipe 2 Cascade rinsing for fragile wafers</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Rinse until message ‘End of rinsing process’ is shown on the touchscreen of the QDR, else repeat the rinsing process.</td>
</tr>
<tr>
<td>34</td>
<td></td>
<td>Substrate drying (WB14) (dry159)</td>
<td>Optional drying step. After the QDR, you can transfer your substrates directly to a Teflon carrier and strip the native SiO₂ in 1% HF (WB15).</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Optional: transfer your wafers directly from the QDR into the 1% HF solution to the native SiO₂.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td><strong>Single substrate drying:</strong></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>1. Use the single-wafer spinner</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Settings: 2500 rpm, 60 sec (including 45 sec nitrogen purge)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>2. Use the nitrogen gun (fragile wafers or small samples)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td><strong>Batch drying of substrates:</strong></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>The Semitool uses the following standard procedure:</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Rinse: 30 sec (600 rpm)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Q-rinse: 10.0 MΩ (600 rpm)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Purge: 10 sec (600 rpm)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>• Drying: 280 sec (1600 rpm)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Note: it is obligatory to apply a single rinsing step in the QDR before using the Semitool!</td>
</tr>
<tr>
<td>35</td>
<td></td>
<td>Etching in 1% HF (etch127)</td>
<td>Purpose: remove native SiO₂ from silicon.</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Obligatory for the silicon</td>
</tr>
</tbody>
</table>
Beaker: 1% HF
Temperature: room temperature
Time = 1 min

This step is obligatory for the MESA+ monitor wafer (if applicable, see Equipment database).

Quick Dump Rinse (QDR)
(#rinse120)

NL-CLR-Wetbenches
Purpose: removal of traces of chemical agents.

Recipe 1 Quick dump rinsing (QDR)
Recipe 2 Cascade rinsing for fragile wafers
Rinse until message ‘End of rinsing process’ is shown on
the touchscreen of the QDR, else repeat the rinsing
process.

Substrate drying (WB15)
(#dry160)

NL-CLR-WB15

Single substrate drying:
1. Use the single-wafer spinner
   Settings: 2500 rpm, 60 sec (including 45 sec nitrogen
   purge)
2. Use the nitrogen gun (fragile wafers or small samples)

Batch drying of substrates:
The Semitool uses the following standard procedure:
• Rinse: 30 sec (600 rpm)
• Q-rinse: 10.0 MΩ (600 rpm)
• Purge: 10 sec (600 rpm)
• Drying: 280 sec (1600 rpm)

Note: it is obligatory to apply a single rinsing step in the
QDR before using the Semitool!

Dry oxidation of silicon
@ 1100°C
(#film191)

NL-CLR-Furnace H1
• Standby temperature: 700°C
• Program: xxxx
• Temp.: 1100°C
• Gas: O2
• Flow: ?l/min

200 nm
thickness.
Oxidation
time = 2
hour 20
min.

Substrate MEMpax
(#subs117)

NL-CLR-Cupboard
Diameter: 100mm
Thickness: 500µm

Dehydration bake
(#litho001)

NL-CLR-WB21/22
Dehydration bake on hotplate
• Temperature: 120°C
• Time: 5min

After the dehydration bake, perform the wafer
priming with minimum delay!
41 ILP Priming HMDS (liquid) NL-CLR-WB21/22 Coating: Primus Spinner • HexaMethylDiSilazane (HMDS) • Spin program: 4000 (4000rpm, 30sec)
42 ILP Coating of Olin OiR 907-17 NL-CLR-WB21 Coating: Primus spinner • Olin OiR 907-17 • Spin program: 4000 (4000rpm, 30sec)
43 ILP Prebake of Olin OiR 907-17 NL-CLR-WB21 Prebake: Hotplate • Temperature: 95°C • Time: 90s
44 ILP Alignment & exposure of Olin OiR 907-17 NL-CLR- EV620 Electronic Vision Group EV620 Mask Aligner • Hg-lamp: 12 mW/cm² • Exposure time: 4sec
45 ILP After exposure bake of Olin OiR resists NL-CLR-WB21 After exposure bake: Hotplate • Temperature: 120°C • Time: 60s
46 ILP Development of Olin OiR resists NL-CLR-WB21 Development: OPD4262 • Beaker 1: 30sec • Beaker 2: 15-30sec
47 ILP Quick Dump Rinse (QDR) NL-CLR-Wetbenches Purpose: removal of traces of chemical agents.
Recipe 1 Quick dump rinsing (QDR)
Recipe 2 Cascade rinsing for fragile wafers
Rinse until message ‘End of rinsing process’ is shown on the touchscreen of the QDR, else repeat the rinsing process.
48 ILP Substrate drying NL-CLR-WB Single substrate drying:
(#dry120) 1. Use the single-wafer spinner
Settings: 2500 rpm, 60 sec (including 45 sec nitrogen purge)
2. Use the nitrogen gun (fragile wafers or small samples)
49 ILP Postbake of Olin OiR NL-CLR-WB21 Postbake: Hotplate resists • Temperature: 120°C • Time: 10min (#litho008)
50 ILP Inspection by optical microscope NL-CLR- Nikon Microscope (#metro101) • dedicated microscope for lithography inspection

etch1208: BHF etch (WB10-private use)
<table>
<thead>
<tr>
<th>Page</th>
<th>Task</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>51</td>
<td>ILP</td>
<td>Etching SiO2 BHF (1:7) (etch125)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NL-CLR-WB9 or 10 Use private beaker with BHF (1:7) Temp.: room temperature Etch depths: • thermal SiO2: 60-80 nm/min • PECVD SiO2: 125 nm/min • TEOS SiO2: 180 nm/min • TEOS H3 (new): 242 nm/min • Pyrex #7740: 20 nm/min • Borofloat BF33: 20-25 nm/min • Si3N4-H2: 0.64 nm/min Etch depth 200 nm. 8 min 40 sec</td>
</tr>
<tr>
<td>52</td>
<td>ILP</td>
<td>Quick Dump Rinse (QDR) (rinse119)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NL-CLR-Wetbenches Purpose: removal of traces of chemical agents. Recipe 1 Quick dump rinsing (QDR) Recipe 2 Cascade rinsing for fragile wafers Rinse until message ‘End of rinsing process’ is shown on the touchscreen of the QDR, else repeat the rinsing process.</td>
</tr>
<tr>
<td>53</td>
<td>ILP</td>
<td>Substrate drying (dry120)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NL-CLR-WB Single substrate drying: 1. Use the single-wafer spinner Settings: 2500 rpm, 60 sec (including 45 sec nitrogen purge) 2. Use the nitrogen gun (fragile wafers or small samples)</td>
</tr>
<tr>
<td></td>
<td></td>
<td><strong>film1532: Sputtering of Tantalum (TCOathy)</strong></td>
</tr>
<tr>
<td>54</td>
<td>ILP</td>
<td>Sputtering of Ta (film622)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NL-CLR-T’COathy Ta Target • Use Ar flow to adjust process pressure. • Base pressure: &lt; 1.0 e-6 mbar • Sputter pressure: 6.6 e-3 mbar • power: 200 W • Deposition rate = 9.4 nm/min Thickness = 10 nm. Time = 1 min</td>
</tr>
<tr>
<td></td>
<td></td>
<td><strong>film1534: Sputtering of Platinum (TCOathy)</strong></td>
</tr>
<tr>
<td>55</td>
<td>ILP</td>
<td>Sputtering of Pt (film624)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NL-CLR-T’COathy Pt Target • Use Ar flow to adjust process pressure. • Base pressure: &lt; 1.0 e-6 mbar • Sputter pressure: 6.6 e-3 mbar • power: 200 W • Deposition rate = 24.0 nm/min Thickness = 190 nm. Time = 7 min 55 sec</td>
</tr>
<tr>
<td></td>
<td></td>
<td><strong>litho1500: Lift-Off with positive resist (WB11)</strong></td>
</tr>
<tr>
<td>56</td>
<td>ILP</td>
<td>Lift-Off (litho500)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>NL-CLR-WB11 Purpose: removal of resist and excess metal from the surface of the substrate by ultrasonication in Acetone. Use the ultrasonic bath in WB11. • Beaker 1: Acetone • Time = 10 min</td>
</tr>
</tbody>
</table>
**Single wafer processing:**
Spray the wafer with Acetone for 30 sec and immediately spray with isopropanol (IPA) for 30 sec.

**Batch wafer processing:**
- Beaker 2: Acetone
- Time = 10 min
- Beaker 3: Isopropanol
- Time = 10 min

**Single substrate drying:**
1. Use the single-wafer spinner
   - Settings: 2500 rpm, 60 sec (including 45 sec nitrogen purge)
2. Use the nitrogen gun (fragile wafers or small samples)

---

<table>
<thead>
<tr>
<th>Page</th>
<th>Process Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>57</td>
<td><strong>Substrate drying</strong> (#dry120)</td>
</tr>
<tr>
<td>58</td>
<td><strong>Cleaning in 99% HNO₃</strong> (#clean005)</td>
</tr>
<tr>
<td>59</td>
<td><strong>Cleaning in 99% HNO₃</strong> (#clean006)</td>
</tr>
<tr>
<td>60</td>
<td><strong>Quick Dump Rinse (QDR)</strong> (#rinse119)</td>
</tr>
<tr>
<td>61</td>
<td><strong>Substrate drying</strong> (#dry120)</td>
</tr>
<tr>
<td>62</td>
<td><strong>Chamber clean Oxford 80 PECVD</strong> (#film194)</td>
</tr>
</tbody>
</table>

---

**film1400: PECVD of SiO₂ - standard (Oxford80)**

<table>
<thead>
<tr>
<th>Page</th>
<th>Process Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>58</td>
<td><strong>Cleaning in 99% HNO₃</strong> (#clean005)</td>
</tr>
<tr>
<td>59</td>
<td><strong>Cleaning in 99% HNO₃</strong> (#clean006)</td>
</tr>
</tbody>
</table>

**Purpose:** removal of organic traces.

- Beaker 1: 99% HNO₃
- Time = 5 min

**Quick Dump Rinse (QDR)** (#rinse119)

**Purpose:** removal of traces of chemical agents.

Recipe 1 Quick dump rinsing (QDR)
Recipe 2 Cascade rinsing for fragile wafers
Rinse until message ‘End of rinsing process’ is shown on the touchscreen of the QDR, else repeat the rinsing process.

**Substrate drying** (#dry120)

**Purpose:**
1. Use the single-wafer spinner
   - Settings: 2500 rpm, 60 sec (including 45 sec nitrogen purge)
2. Use the nitrogen gun (fragile wafers or small samples)

**Chamber clean Oxford 80 PECVD** (#film194)

**Purpose:**
- Chamber clean
<table>
<thead>
<tr>
<th>Page</th>
<th>Process</th>
<th>Details</th>
</tr>
</thead>
</table>
| 63   | PECVD of SiO₂ Standard | NL-CLR-OXFORD Plasmalab 80⁺
Apply purge sequence before and after use
Purge sequence: 1 min N₂, pump down, apply three times
Parameters:
- Electrode temp. = 300°C
- 2% SiH₄/N₂ flow = 200sccm
- N₂O flow = 710sccm
- pressure = 650mTorr
- APC = 33
- power LF = 60W
- Deposition rate= 35-40 nm/min
Thickness = 1000 min.
Time = 30 min. |
| 64   | Chamber clean Oxford 80 PECVD | NL-CLR-Oxford 80 PECVD
- Chamber clean |
| 65   | Ellipsometer measurement | NL-CLR-Woolam M-2000 ellipsometer |
| 66   | Inspection of LPCVD/PECVD layers | NL-CLR-cold light source
Particle and haze inspection of LPCVD/PECVD layers using a cold light source.
Procedure: use streaking light for inspection.
Contact: Ite-Jan/Chris for results. |

**litho1801: Lithography of Olin OiR 907-17 (positive resist - ILP)**

<table>
<thead>
<tr>
<th>Page</th>
<th>Process</th>
<th>Details</th>
</tr>
</thead>
</table>
| 67   | Dehydration bake | NL-CLR-WB21/22
Dehydration bake on hotplate
- Temperature: 120°C
- Time: 5min
After the dehydration bake, perform the wafer priming with minimum delay! |
| 68   | Priming HMDS (liquid) | NL-CLR-WB21/22
Coating: Primus Spinner
- HexaMethylDiSilazane (HMDS)
- Spin program: 4000 (4000rpm, 30sec) |
| 69   | Coating of Olin OiR 907-17 | NL-CLR-WB21
Coating: Primus spinner
- Olin OiR 907-17
- Spin program: 4000 (4000rpm, 30sec) |
| 70   | Prebake of Olin OiR 907-17 | NL-CLR-WB21
Prebake: Hotplate
- Temperature: 95°C
- Time: 90s |
| 71   | Alignment & exposure of Olin OiR | NL-CLR- EV620
Electronic Vision Group EV620 Mask Aligner
MASK 3 |
After exposure bake of Olin OiR resists

- Hg-lamp: 12 mW/cm²
- Exposure time: 4sec

Development of Olin OiR resists

- After exposure bake: Hotplate
  - Temperature: 120°C
  - Time: 60s

Quick Dump Rinse (QDR)

- Temperature: 120°C
- Time: 60s

Quick Dump Rinse

Recipe 1 Quick dump rinsing (QDR)
Recipe 2 Cascade rinsing for fragile wafers
Rinse until message ‘End of rinsing process’ is shown on the touchscreen of the QDR, else repeat the rinsing process.

Substrate drying

Single substrate drying:
1. Use the single-wafer spinner
   Settings: 2500 rpm, 60 sec (including 45 sec nitrogen purge)
2. Use the nitrogen gun (fragile wafers or small samples)

Postbake of Olin OiR resists

- Temperature: 120°C
- Time: 10min

Inspection by optical microscope

Dedicated microscope for lithography inspection

etch1511: Etching of SiO₂ or SiN: C-Ar/CHF₃ (AdixenSE)

- Argon (sccm) 100
- CHF₃ (sccm) 100
- APC % 100
- ICP (Watt) 1200
- CCP (Watt) LF 150 (Vdc=680V)

Etch time 4 min and 30 sec.
<table>
<thead>
<tr>
<th>Page</th>
<th>Section</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>79</td>
<td>ILP</td>
<td>Stripping of Positive Resist ((strip130))</td>
</tr>
</tbody>
</table>
|      |         | Etch rates: SiO2: 250nm/min - SiRN: 300nm/min - Si: 70-80 nm/min  
|      |         | Resist: 160nm/min - SU8: 150nm/min  
|      |         | NL-CLR-TePla360  
|      |         | Purpose: Stripping of Positive Resists on specific metals in O2/H2 Plasma  
|      |         | **Recipe 041**  
|      |         | O2 flow: 250sccm  
|      |         | H2 flow: 250sccm  
|      |         | Pressure: 0.7mbar  
|      |         | Power: 800Watt  
|      |         | Time: 10min  
| 80   | ILP     | Cleaning in 99% HNO3 (#clean005) |
|      |         | NL-CLR-WB16  
|      |         | Purpose: removal of organic traces  
|      |         | • Beaker 1: 99% HNO3  
|      |         | • Time = 5 min  
| 81   | ILP     | Cleaning in 99% HNO3 (#clean006) |
|      |         | NL-CLR-WB16  
|      |         | Purpose: removal of organic traces  
|      |         | • Beaker 2: 99% HNO3  
|      |         | • Time = 5 min  
| 82   | ILP     | Quick Dump Rinse (QDR) (#rinse119) |
|      |         | NL-CLR-Wetbenches  
|      |         | Purpose: removal of traces of chemical agents  
|      |         | Recipe 1 Quick dump rinsing (QDR)  
|      |         | Recipe 2 Cascade rinsing for fragile wafers  
|      |         | Rinse until message ‘End of rinsing process’ is shown on the touchscreen of the QDR, else repeat the rinsing process  
| 83   | ILP     | Substrate drying (#dry120) |
|      |         | NL-CLR-WB  
|      |         | **Single substrate drying:**  
|      |         | 1. Use the single-wafer spinner  
|      |         | Settings: 2500 rpm, 60 sec (including 45 sec nitrogen purge)  
|      |         | 2. Use the nitrogen gun (fragile wafers or small samples)  
| 84   | ILP     | Wafer bonding (#bond133) |
|      |         | NL-CLR-Furnace E2  
|      |         | Application: silicon-glass bonding with Ta/Pt electrodes  
|      |         | • Standby temperature: 400 °C  
|      |         | • Program:  
|      |         | • Temperature range: 600-650 °C  

**bond1107: Wafer bonding silicon-glass with Ta/Pt structures (E2)**

- **Cleaning in 99% HNO3 (#clean005)**
  - NL-CLR-WB16
  - Purpose: removal of organic traces
  - • Beaker 1: 99% HNO3
  - • Time = 5 min
- **Cleaning in 99% HNO3 (#clean006)**
  - NL-CLR-WB16
  - Purpose: removal of organic traces
  - • Beaker 2: 99% HNO3
  - • Time = 5 min
- **Quick Dump Rinse (QDR) (#rinse119)**
  - NL-CLR-Wetbenches
  - Purpose: removal of traces of chemical agents
  - Recipe 1 Quick dump rinsing (QDR)
  - Recipe 2 Cascade rinsing for fragile wafers
  - Rinse until message ‘End of rinsing process’ is shown on the touchscreen of the QDR, else repeat the rinsing process.
- **Substrate drying (#dry120)**
  - NL-CLR-WB
  - **Single substrate drying:**
  1. Use the single-wafer spinner
     - Settings: 2500 rpm, 60 sec (including 45 sec nitrogen purge)
  2. Use the nitrogen gun (fragile wafers or small samples)
- **Wafer bonding (#bond133)**
  - NL-CLR-Furnace E2
  - Application: silicon-glass bonding with Ta/Pt electrodes
  - • Standby temperature: 400 °C
  - • Program:
  - • Temperature range: 600-650 °C
back1100: Dicing of a silicon wafer

85  ILP  Dicing foil Nitto SWT 10
(#back103)

86  ILP  UV dicing foil (Adwill D-210)
(#back104)

87  ILP  Dicing of a Silicon wafer
(#back101)

• Gas: N₂
• Flow: xx l/min
• Ramp: xxx°C/min
• Cooldown: xxx°C/min

---

Dicing of a silicon wafer

Dicing foil Nitto SWT 10
Nitto SWT 10 dicing foil

UV dicing foil (Adwill D-210)
Information:
- Thickness: 125μm
- Material: 100μm PET + 25μm Acrylic (adhesive)
- Adhesion before UV: 2000 mN/25mm
- Adhesion after UV: 15 mN/25mm
- UV irradiation: Luminance > 120mW/cm² and Quality > 70mJ/cm² (wave length: 365nm)

Dicing of a Silicon wafer

Applications:
- Silicon wafers, bonded silicon-silicon wafers (max 1.1mm)
- See #back103 for laminate of Nitto STW T10 dicing foil (80 μm)
- See #back104 for laminate of UV dicing foil (125μm)

Parameters dicing:
- Wafer work size: 110 mm for a standard 100 mm silicon wafer
- Max. Feed speed: 10 mm/sec
- X, Y values: correspond respectively to Ch1 and Ch2 and those values are determined by mask layout
- Saw type NBC-Z 2050
- Select in blade menu: NBC-Z-2050

Blade info:
- Exposure: 1.3 mm (maximum dicing depth for a new blade)
- Width: 50 um
- Spindle revolutions: 30,000 rpm

Depth settings:
- Maximum cut depth: 1.1 mm
- Foil thickness: See foil info
- Min. blade height: 50 μm
REFERENCES SUPPLEMENTARY INFORMATION