The sensors for the intelligent micro washing system

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1. Introduction

After the global view on the project described in the first two work reports, it is now necessary to start a more structural evaluation. In this third work report the demanded sensing principles are coupled to the technology.
There are several parameters that can be measured using only thin (metal) films. It is not obvious that the use of ISFET-based sensors is more reliable or convenient. It should be evaluated which technologies are available and what they can offer. From this evaluation it might come clear what advantage in sensing parameters can be obtained by combining materials.

In the recently proposed contract a more fundamental project description was given:

> The integrated washing sensor project:
>
> The Ph.D. research aims at the development of an integrated sensor, for the control of washing processes, with the use of active elements in order to examine as many functions as possible with a minimum number of measuring elements by using these in different modes scheduled by a micro controller. This means that one sensor must be able to determine as many parameters as possible. Those parameters can be temperature, pH, conductivity, dynamic surface tension, bleach activity (potentiometry/ amperometry) and soil level of the system.
> Attention must be paid to the possibilities on error detection and error diagnose of the sensor. By this, the current shortcomings of the usage of sensors in washing machines, like soil deposition on the sensor, limited robustness and costs, hopefully will be overcome. Theoretically it seems possible to implement such a sensor by integration of ISFET-technology based sensors and measuring techniques.

To my opinion it is more convenient to speak of a sensor array containing N sensors that can perform more than N measurements. This is a more structural point of view than the one in the project description. The mentioned error considerations will consist of the evaluation of the drift and calibration behaviour of the sensors.
The description doesn't say anything about the application of the sensor. The sensor will be used to control the washing process so the parameters to be measured must be controllable. With each measured value it should be considered:

- What washing parameter it represents (conductivity doesn't say anything unless it is correlated to the rinsing effectiveness for example);
- If it is possible to control this parameter

So the choice of which sensors will be integrated is very complicated and will depend on the progresses of the Unilever research concerning the other aspects of an automatic dosing system.

2. Classification by technology

In this section a comparison is made between technologies. First the cheapest option is chosen. This is the case in which only deposition and patternation is allowed. The summary is made with only thin film technology in mind, but thick film methods can be used aswell. After that an overview is given of what is possible if diffusion areas are allowed.
In the summary, structures are mentioned with their modes of operation. An operation mode can be defined as a connection, frequency range or signal range from which different information can be obtained than using other modes. The operation modes are the key to integrating functions on one structure.

2.1. The price of a device

It is very hard to say something about the price of a device produced with a certain technology. This price depends on:

- The yield of the process;
- The used wafer area;
- The process time;
- The required machines;

If the number of masks is taken as an indication of the process time, the ratio of thin-film versus MOS is about 2 : 6. A MOS process, however requires more expensive technology and will have a lower yield because of the larger number of masks.

Another financial problem can be the availability of the processes. If a company like Unilever does have the evaporation and lithography machines and are not able to do the diffusion, the metal film sensors will be much more cheaper and more flexible.

2.2. Patterning and evaporation only

First assume that only depositing and patterning of materials is allowed. The technology can be either thin film (silicon technology), thick film or macro technology (for example metal electrodes). Available materials are summarized in table 2.1.

Table 2.1: Materials that can be applied using deposition and patterning

Material	Examples	Deposition	Patterning
Metal	Al, Au, Pt, Cu, ...	Evaporation	Lift off, wet etching
Semiconductors	Si	Polysilicon	Wet etching
Oxides	Ta_2O_5, IrOx, SiO_2, ...	Evaporation + oxidation	Patterning of metal before oxidation
Polymers	PVC, Polysiloxane	Polymerisation	Photolithography after adding photo initiator

2.2.1. Metal films

Physical methods

With the physical methods the aim is to avoid electrochemical modifications and to get information from physical properties.

A - Current through a metal strip

Set-up: Metal strip
Applied signal: Voltage
Measured: Current
Frequency: Low
Information: Temperature

An example is the Pt-100 element [1]. The Pt-100 uses the thermoresistive effect of a platinum strip of 100W. Such a strip has over a moderate range of temperature a nearly proportional resistive behaviour, the resistance can be written as:

$$R_T = R_0[1 + \alpha(T - T_0)] \qquad (2.2.1.1)$$

with R_0 the resistance at T_0 and a the temperature coefficient at T_0. For platinum the factor a is 0.00392 $°C^{-1}$. Platinum resistance thermometers have a linearity of ±0.2% and are capable of an accuracy of 0.001°C over the range of 0-100°C. For larger temperature ranges some well fitted quadratic equations can be used. The application of a platinum strip as a temperature sensor is generally done in a bridge configuration.

B - Current through the liquid

Set-up: Two contacts
Applied signal: Sine current
Measured: Voltage
Frequency: Moderate (1-100kHz)
Information: Conductance

An examples is the interdigitated finger structure (two points conductivity set-up). The problem with this device is that the interface potential is part of the current loop, so this gives an error in the measured conductance. An improvements is the four points set-up.

C - Electrolyte potential measurement

Set-up: Four contacts
Applied signal: Sine current on outer electrodes
Measured: potential on inner electrodes
Frequency: Moderate (1-100kHz)
Information: Conductance

Now the measured potential is in a circuit with zero current.

Electrochemical methods, controlled potential

Electrochemical experiments can be performed using two electrodes. The reactions will take place at both electrode-liquid interfaces and both will be visible in the measured value. To monitor the behaviour of only one electrode a three electrode system is necessary (potentiostat). In the development stage a potentiostat will be used, in the final application a two electrode set-up is more convenient.

D - Chrono-amperometry

Set-up: Two electrodes or potentiostat (three electrodes)
Applied signal: Single potential step
Measured: Current in time
Frequency: High because of fast step
Information: Concentrations, Faradaic and non-Faradaic information

After applying a positive potential-step to a working electrode the electrochemical equilibrium

$$\mathrm{Red} \leftrightarrow \mathrm{Ox} + \mathrm{e}^- \qquad (2.2.1.2)$$

moves to the right. If the current is monitored, this experiment is referred to as chrono-amperometry. In case of a process under diffusion control and immediate complete depletion of the reactant, the current is described by the Cottrell equation [2]:

$$i(t) = nFAC_{Ox}\sqrt{\frac{D_{Ox}}{\pi t}} \qquad (2.2.1.3)$$

with n the number of electrons transferred, F the Faraday constant (9.64867×10^4 C/mole), A the interface surface, C the bulk concentration and D the diffusion constant.

If the diffusion constants are known, the Cottrell equation can be used to determine the concentration H_2O_2 from a chrono-amperometric experiment [3]. This is interesting because hydrogen peroxide is an important bleach chemical.

$$H_2O_2 \leftrightarrow O_2(g) + 2H^+ + 2e^- \qquad \text{-0.682 V} \qquad (2.2.1.4)$$

This method is well developed in glucose sensors where a GOD-membrane catalysis the glucose concentration to a hydrogen-peroxide concentration. Because the only changes in the membrane are the H_2O_2-concentration a selectivity is guaranteed. In the washing sensor the bulk concentration hydrogen-peroxide must be measured so the membrane can be omitted and the selectivity will be a problem.

Just after the fast potential step, the surface double layer is filled with charge. This gives a fast exponential current response called the non-Faradaic charging. Secondly the diffusion limited Faradaic processes become more important.

E - Sampled-current voltammetry

Set-up: Two electrodes or potentiostat (three electrodes)
Applied signal: Multiple potential steps
Measured: Current after time t
Frequency: High because of fast steps
Information: Faradaic processes information

Now a large number of chrono-amperometric experiments are performed with increasing amplitude and the current is sampled after time t. A graph is made of The sampled current versus the step size. This technique is the base of polarography (voltammetry at a dropping mercury electrode), which is harder to realize in a small set-up.

F - Double potential step chrono-amperometry

Set-up: Two electrodes or potentiostat (three electrodes)
Applied signal: Potential step up followed by a potential step down
Measured: Current in time
Frequency: High because of fast step
Information: Concentrations, Faradaic and non-Faradaic information

This is interesting because it is a reversal technique.

G - Polarographic methods

Set-up: Dropping mercury electrode
Information: Concentrations

With a DME (Dropping Mercury Electrode) it is possible to do a number of polarographic experiments. These are techniques to reduce the relative contribution of charging currents. Because of the complex set-up less interesting for application in a sensor array.

H - Coulometry

Set-up: One of the amperometric types
Information: Charge flow, Faradaic and non-Faradaic

By taking the integral of the current flow in the previous controlled potential experiments, the passed charge is obtained:

$$Q(\tau) = \int_{t=0}^{t=\tau} Idt \qquad (2.2.1.5).$$

I - Potential sweep methods

Set-up: Two electrodes or potentiostat (three electrodes)
Applied signal: Potential triangle
Measured: Current in time
Frequency: Low, slope = 100 mV/sec
Information: Concentrations, Faradaic information

The most common example is Cyclic Voltammetry. With these methods a fingerprint of the electrolyte is obtained. The interest is especially in the development stage of the sensor.

Electrochemical methods, controlled current

The instrumentation for controlled current experiments is simpler than the potentiostats required in the controlled potential ones, since no feedback from the reference electrode to the control device is required [2]. Usually the mathematics involved in solving the diffusion equations are much simpler aswell.

J - (Constant current) chrono potentiometry

Set-up: Two or three electrodes
Applied signal: Current step
Measured: Potential
Frequency: High, fast step
Information: Concentrations, non Faradaic and Faradaic information

After applying a constant current to a metal electrode, the electroactive species in the electrolyte will be reduced. The potential of the electrode moves to potentials characteristic for the electroactive couple. After depletion of one species the potential rises until another electrochemical reaction is found.

The diffusion system is described by the Sand equation [2]. The time to reach depletion is called the transition time and is proportional to the diffusion constant and the square of the concentration.

K - Programmed current chrono potentiometry

Set-up: Two or three electrodes
Applied signal: Current ramp
Measured: Potential
Frequency: Low
Information: Concentrations, Faradaic information

L - Current reversal and cyclic chrono potentiometry

Set-up: Two or three electrodes
Applied signal: Current step
Measured: Potential
Frequency: High, fast step
Information: Concentrations, non Faradaic and Faradaic information

After one current step the current is reversed after some time. If this is done repeatedly it is referred to as cyclic chronopotentiometry.

M - Charge step method (coulostatic impulse)

Set-up: Two electrodes
Applied signal: Current pulse (0.1-1µsec)
Measured: Open circuit potential
Frequency: High, fast pulse
Information: Charging of electrical double layer

With the charge step method a fast current pulse is

N - Control of local pH

Combination of physical and electrochemical principles

O - Bubble electrodes

Set-up: Working electrode and counter
Applied signal: Current
Measured: Overpotential
Frequency: Low
Information: Dynamic surface tension, surfactant

The development of a dynamic surface tension sensor is currently performed (Alex Volanschi). The device consists of a current controlled working electrode which generates gas bubbles. From the fluctuations in the over potential the bubble frequency can be determined. It seemed that this frequency is proportional to the surfactant concentration.
The DST electrodes are not simple metal films. There are two configurations. First the cavity electrode which requires an anisotropic etch of silicon (KOH), the bubble nucleation is controlled here by the shape of the electrode. Secondary the gas nucleation (air bag) electrode where the nucleation is controlled by an instantaneous amount of gas, this device requires an isotropic etch of silicon.
The problem with this electrodes is that the model is not yet finished, the bubble-frequency/surfactant-concentration relation is surfactant-type dependent so a calibration curve is needed.

Other methods

P - Faradaic Impedance methods

Set-up: Waveform generator, potentiostat, I-V converter, filters
Applied signal: Voltage slope with AC-signal
Measured: Small signal magnitude and phase
Frequency: Moderate
Information: Low concentrations

The most used impedance method is AC-polarography, which is called AC-voltammetry if a dropping mercury electrode is used. With AC-polarography a slowly scanned DC value is summed with a small AC-value (some mV). The measured values are the magnitude and phase of the AC-current as a function of the frequency.
Detection limits for polarographic methods can reach 10^{-7}M. An effective discrimination between Faradaic and non-Faradaic properties is possible.

Q - Stripping methods

Set-up: One of the electrochemical methods listed above
Information: Bulk analysis, very low concentrations

The previous described methods monitored the reactions just at the surface of the working electrode. With stripping analysis, electrolysis is used to preconcentrate a material on the surface of an electrode, before a voltammetric analysis. In this way information about the bulk of the fluid is obtained and very low concentrations can be detected.

2.2.2. Semiconductors

The electron transfer across a semiconductor/liquid interface can easily be understood by looking at the energy levels [4]. The behaviour is dependent on the overlap between energy levels in the liquid and the solid. A semiconductor has a forbidden band gap region, and so only electrons from the valence and the conduction band can interact with the liquid. This results in small currents because the overlap is small. These conditions lead to a rectifying behaviour.
When a semiconductor is completely depleted at the surface, an insulator/liquid interface is obtained [5] similar to the situation that will be described in subsection 2.2.3A.
In literature only a small number of applications of semiconductor/liquid interfaces are reported. Solid state sensors based on semiconductor/liquid interfaces were not found.

2.2.3. Oxides

A - Insulating oxides

In conductor/liquid interfaces the potential drop was mainly across the Helmholtz layer, in insulator/liquid interfaces the potential drop will be across the insulator. Because of the insulating layer only capacitive measurements, like conductance [6], can be performed.
On insulating surfaces charge adsorption can take place and redox interference becomes less dominant [5]. The adsorbed charges in water are mainly H^+ and OH^- which have an equilibrium with the sites on the surface. An important phenomenon is

ion exchange with which an adsorbed H^+ or OH^- ion is exchanged with an other ion from the solution depending on it's concentration.

All semiconductor oxides are good insulators (unless the thickness is smaller than the tunnelling distance of electrons). Silicon oxide (SiO_2) is an insulator which is easy to obtain in silicon processes.

Tantalum oxide (Ta_2O_5) is also an insulator but has a lot more sites than Silicon oxide. The Ta_2O_5/solution interface has a stable relatively low impedance which is almost completely determined by the activity of protons in the solution. So noise caused by interfering redox processes is reduced.

B - Conducting oxides

Iridium oxide is a conductor, so all electrochemical methods listed in the metal/liquid section can be performed. In the iridium oxide film both Ir^{3+} and Ir^{4+} are present. The ratio can be controlled electrochemically, but the total amount is constant. The electrochemical properties of an IrOx-film are completely different from metal films.
Generally at conducting electrodes redox sensitivity is very high, iridium oxide however is a good conductor but shows a low An application is the controlled injection of protons from the IrOx film into the electrolyte.

2.2.4. Polymers

Polymers like PolyVinylChloride (PVC) and polysiloxane are permeable to ions and gasses, so those polymers can be evaluated as being solid electrolytes [5]. The interface will be between two ionic conductors. Some other not-polymeric materials like ZrO_2 and LaF_3 show a similar behaviour. The advantage of those materials is in the possibility to make ion sensitive electrodes (ISE's).

As an example the fabrication of an ion selective PVC membrane is mentioned here. The polymerisation is done from a cocktail containing the following contaminents:

a Solvent: Tetrahydrofuran (THF);
b Membrane matrix: PolyVinylChloride (PVC);
c Plasticizer;
d Ionophore;
e Additive: SodiumTetraPhenylBorate (NaTPB).

Normally the amounts of contaminents b, c and d are 33 : 66 : 1 wt% (together 0.1g solved in 0.75 ml THF). After evaporation of the solvent the membrane consists of a solid matrix holding the ionophore and the additive.
Ionophores are ion selective molecules and the additive is present to charge the membrane in order to pull in ions. The proper operation of the membrane is based on the buffering behaviour of the additive/ionophore combination.
In a future work report the development of a calcium sensitive membrane for the use with an ISFET will be described.

2.3. Adding diffusion areas

Now we assume that diffusion steps are allowed aswell (besides the evaporation and patterning of materials mentioned in the previous section). While in the previous section the realization could be in either thin-film, thick-film or macro electrodes, now we are restricted to using silicon technology.
Using diffusion areas, pn-junctions and so transistors can be made. This allows a much wider range of sensors, for example ISFET based devices. The mode of operation can be divided in:
- Interaction with the liquid or not
- Operation frequency

Table 2.2: Structures using diffusion areas and film deposition

Structure	Examples	Modes
Doped region		Current from silicon to liquid
Single pn-junction	Temperature, transistor technique	Current in diode only, current to liquid
Bipolar transistors	PTAT, on chip electronics	No interaction with liquid
MOS transistors	PTAT, on chip electronics	No interaction with liquid
ISFETs	pH, potential measurement, ...	Interaction with liquid, low or high frequency
ChemFET	ISE	Interaction with liquid, low frequency

2.3.1. Doped region

This is a expansion of the semiconductor/liquid interface mentioned in section 2.2.2. If the semiconductor is doped the application is more convenient because the behaviour is controlled. It was told that the interface behaves like a pn-junction. By adding more positive or negative charge the semiconductor begins to behave more like a metal.
Applications of doped semiconductors can be found in the capacitive methods like impedance measurements.

2.3.2. Single pn-junctions

A - Using the current in the silicon
In work report 1 the temperature dependency of a pn-junction was mentioned. When the currents are restricted to the bulk of the silicon (so no current flow to the liquid), a temperature measurement can be performed.

B - Using the current from silicon to the liquid
A technique called "transistor technique" is sometimes used to evaluate electrode reactions because valence band electrons and conduction band electrons can be detected separately [4]. In this set-up only the n-type region is in contact with the liquid, the p-type layer is covered by the n-region.

2.3.3. Bipolar transistors

A better temperature sensor is obtained with the PTAT (proportional to the absolute temperature) configuration as shown in work report 1. This requires four transistors. From literature no transistors in contact with liquids were found.

2.3.4. MOS transistors

With MOS transistors the same remarks as with the bipolar transistors are true. An advantage is that the MOS process looks more like the ISFET process than a bipolar process.

2.3.5. ISFETs

A - Low frequency
This is the most common ISFET mode. The device is placed in a circuitry in which the drain current and the drain-source potential are held constant, so this is a low frequency mode. The output potential is related to the H^+ concentration.

B - High frequency
With a higher frequency information can be determined about the conductivity of the liquid [7].

C - Potential sensing
With ISFETs in the input stage of a differential amplifier, a potential difference in the liquid can be determined. An example is the four points conductivity measurement using two ISFETs [8].

2.3.6. ChemFETs

The use of solid electrolytes mentioned in section 2.2.4 can be expanded using an ISFET. If the ion selective polymer is placed on an ISFET a ChemFET is obtained with which a more sensitive ion detection can be performed.

2.4. Results

In the previous sections techniques, operation modes and materials were mentioned in a certain sequence. The next overview gives a list of the subsection titles, the used font gives information about what it represents:

fabrication technique
Used materials
measure method
operation mode.

Patterning and evaporation only

Metal films
Physical methods
- A - Current through a metal strip
- B - Current through the liquid
- C - Electrolyte potential measurement

Electrochemical methods, controlled potential
- D - Chrono-amperometry
- E - Sampled-current voltammetry
- F - Double potential step chrono-amperometry
- G - Polarographic methods
- H - Coulometry
- I - Potential sweep methods

Electrochemical methods, controlled current
- J - (Constant current) chrono potentiometry
- K - Programmed current chrono potentiometry
- L - Current reversal and cyclic chrono potentiometry
- M - Charge step method (coulostatic impulse)
- N - Control of local pH

Combination of physical and electrochemical principles
- O - Bubble electrodes

Other methods
- P - Faradaic Impedance methods
- Q - Stripping methods

Semiconductors
Oxides
- A - Insulating oxides
- B - Conducting oxides

Polymers

Adding diffusion areas

Doped region
Single pn-junctions
- A - Using the current in the silicon
- B - Using the current from silicon to the liquid

Bipolar transistors
MOS transistors
ISFETs
- A - Low frequency
- B - High frequency
- C - Potential sensing

ChemFETs

The next step is to find operation modes of one geometrical structure that can be used together in order to get more information about the environment.
Consider only the "Patterning and evaporation only" part. If more functions using only one structure (material) is desired we must look in the previous list under one underlined header and choose different operation modes or techniques.
For the "adding diffusion areas" part a similar use of this list is possible. However, the combination of items from the "adding diffusion areas" and "Patterning and evaporation only" lists is more complicated.

3. Materials endure test in a washing machine

The devices will be used in a washing machine, so their environment will be a base liquid with elevated temperature in the presence of active chemicals (bleach enzymes). Some existing devices were selected and placed in a washing machine. In this way some many-used silicon technology materials were qualitatively tested.
The materials are:

- Aluminium (Al);
- Platinum (Pt);
- Gold (Au);
- Silicon oxide (SiO_2);
- Iridium oxide;
- Pt with Ta_2O_5;
- Al with Ta_2O_5;

Packaging materials:

- Hysol;
- Polyimide;

The used machine is a Zanussi Intimat de luxe which is of the type twin tub, top loader. The devices were packaged with Hysol on a printed circuit board and placed on the heating element some centimetres from the outlet of the tub.

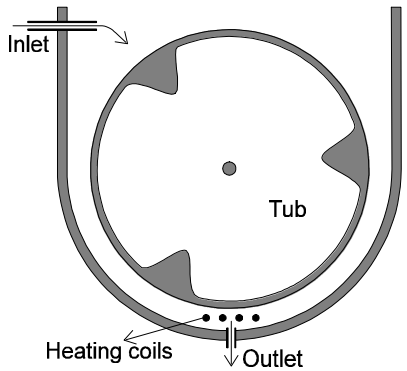

Figure 3.1: Structure of the washing machine

The devices stayed there one week in which four washing programs were performed:

Table 3.1: Performed washing cycles

Program	**Temp [°C]**	**Detergent**
D4 Wool wash	30	Dreft colour
E5 Short programm	60	Dobbelman
BE Coloured wash without pre-wash	40	Dreft colour
E5 Short programm	40	Dreft colour

The materials were optically inspected before and afterwards. The Hysol showed a modification of the surface. From a clear glue it changed to a white covered, non

scratchable material. Obviously it can't sustain a base environment. The situation was not a reason to conclude that Hysol can't be used to package the devices.
None of the other materials showed a chemical modification. Only some mechanical scratches were visible.

4. Future work

Now a number of materials, techniques and operation modes for sensor design are summarized, some conclusions must be found. The aim is to find nice combinations of operation modes using only one structure, or more generally speaking: a number of N sensors which can measure N+M parameters. A second option is that the information obtained by the combination of sensors is used to improve reliability.
The list of sensing principles is far from complete. Probably some more options will be found, so the list will be expanded during the next months.

The first practical work will be performed to get more feeling about the sensing principles. Currently an Italian student (Sergio Botti) is doing a four months assignment on chrono-amperometric concentration determinations [3]. This is to learn about electrochemical methods.
Secondly I am preparing some experiments in order to make a calcium sensitive PVC membrane to put on an ISFET. This will be done using commercially available ionophores. The project is interesting to learn about ISFETs and selective membranes and to obtain a hardness sensor.

In future the materials endure experiment will be repeated in a quantitative way. Some resistor structures are being processed. These can be measured before and after washing. This gives a more reliable view on the surface modification.

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