The development of sensor arrays for an intellingent micro washing system

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objective

In conventional washing processes, the operator adds a certain amount of detergent to the laundry and chooses a machine program and a washing temperature. After the washing program is completed, the wash is inspected with human sensors (eyes, nose and hands). According to the obtained parameters a decision is made whether the result is satisfying or not. Important criteria are the brightness and the smell of the laundry. When the result is not sufficient, the next washing cycle will be performed with adapted inputs (more or less detergent, other program). However, if the result is judged as sufficient, a human operator will never know if the laundry was already clean ten minutes earlier.

It can be questioned whether or not it will be possible to replace the human sensors by electronic sensors which will give an independent decision on the output cleanness of the laundry. While the human operator is not able to examine the laundry during the washing process, such sensors can give an on-line monitoring of the situation in the tub. The advantage is that during the washing process this process can be adapted and an objective decision can be made at what time the wash is clean.

Although the intelligent human sensors can never be replaced by artificial ones, we nevertheless have to satisfy the procedure with an array of realistic sensors from which output signals decisions can be made which are comparable to the human analysis. In this work report, a decision is made about the parameters necessary to monitor the washing process and an analysis is given on how integration of the required sensors can be realised.

Table of contents (short version):

Table of contents (long version):

1. Introduction

In literature some nice methods are reported which combine sensors to find more information than using some separate sensors. If a sensor gives an absolute value of parameter A, and another gives a relation of this parameter A relative to parameter B, then the combination of these sensors may give absolute information on parameter B.

An example is the measurement of lung volume, where an electrical impedance measurement on both sides of the chest gives a relation between right and left lung volume. This is a simple but relative measurement which has unfortunately no direct physiological significance. In combination with a spirometer, which gives an absolute value for the total volume of both human lungs, the absolute volume of the separate lungs can be calculated [1].

Another example is the gas flow sensor [2] where thermoresistive bridges are used to measure gas flow in two ways. The first method uses a standard anemometric sensor principle and the other a thermal time of flight set-up. Since these two act on a different way on gas parameters, it is possible to get information on both the mass flow and the gas mixture.

Interesting can be the choice between autonomous good systems and multiple less good systems. A technique called polygraphy is a certain medical method where the combination of various known medical instrumentation techniques gives more information about the condition of a patient than with the separate instruments [3]. This view on measuring can be the guideline for the development for a sensor array for monitoring washing processes.

1.1. The aim of this report

With single sensor applications, problems with calibration and references are experienced generally. By combining sensors in one set-up and using smart measuring methods, these problems might be solved because the information obtained from the separate sensors is coupled to form a new set of parameters.
With this report a structural method is performed to find such a combination of sensor principles that calibration and reference problems are being eliminated. Besides that, the combination might give new information on parameters which are not measurable with a single sensor.
To find such combinations, a variety of existing sensors and measurement methods is listed from three points of view. First the methods found in literature are listed in the order of the complexity of the used technology. The second viewpoint starts from the electronic device that is being modulated by the measured parameter. To satisfy the request of designing washing sensors, a list is given of the most important methods to measure washing parameters.

When the overview is made complete, these three lists will contain the same sensors and methods in three different contexts. This will give a three-axis impression of possible subdivisions. Figure 1.1 gives a view of this three dimensional vision with the PT100 temperature sensor and the interdigitated finger structure (conductivity sensor) as an example.

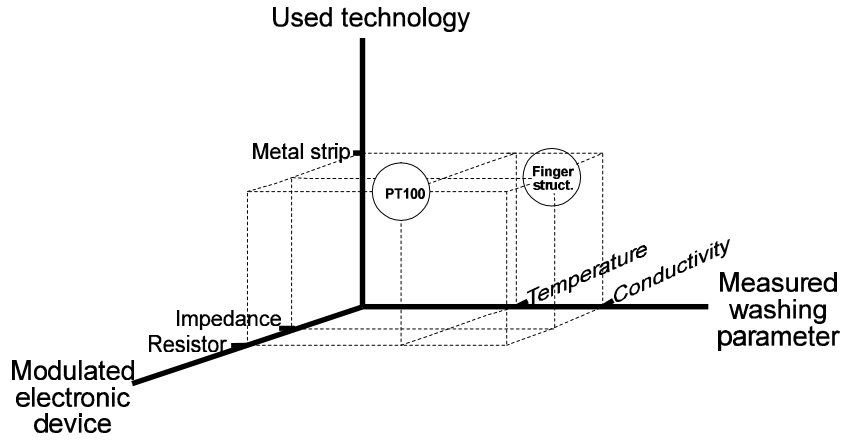


Fig. 1.1: Existing sensors and methods in a three dimensional area

From this impression:

- Methods that can be performed using a single technology can be found. A metal strip, for example, can be used to measure temperature and perform electrochemical methods as well.
- Missing parts in the maze will become clear. If there are chemical dependent resistors and capacitances, where are the chemical sensitive inductors?
- Advantages of methods become clear. Can a relative method be combined with an absolute measurement?

The objective is to find subdivisions of sensor principles that use a similar technology and that give an improvement in relation to the separate sensors.

1.2. The structure of this report

Before starting a structural overview on a large number of available physical and chemical sensors, this report lists some basic ideas and terminology on sensing principles in chapter 2.

In the subsequent chapters three qualifications of sensors are made from three different point of views. The choice of these views is based on a certain vision on sensors.
A sensor is a device which converts information from a certain domain to a domain which can be interpreted by humans or control logic. For the sensors described in this report, the first domain will be that of physical and chemical properties in electrolytes, the second domain is in almost all the cases the electronic one.
Generally, a sensor consists of a recognizing part, which either makes a parameter of a second part varying with an input signal or converts energy from the input domain to

this second part (figure 1.2). The first part will be called here the receptor, the second part is referred to as the modulated electronic device.

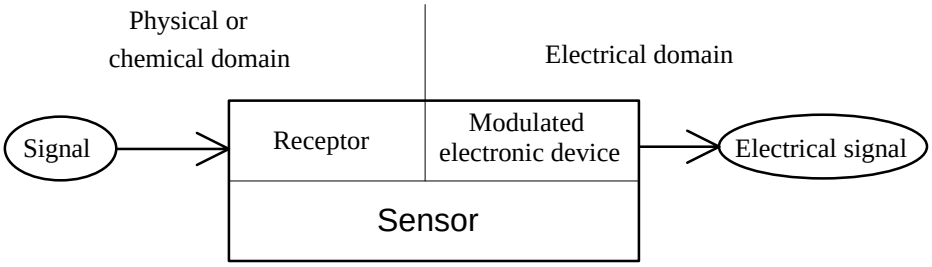


Fig. 1.2: Basic structure of a sensor

In many cases, the receptor part is just a material which properties are used for the (selective) sensing. For example, the ISFET has a Ta_2O_5 layer which makes the threshold voltage of a modified MOSFET varying with the pH. The Ta_2O_5 layer is here the receptor, and the transistor the modulated electronic device. Some more examples are summarized in table 1.1.

Table 1.1: Some sensors described in the terminology of figure 1.2

Sensor	Measured parameter (Chapter 4)	Transducing principle of receptor part (Chapter 3)	Modulated electronic device (Chapter 5)
ISFET	pH	Ta_2O_5 - layer: pH ® V_T	MOSFET
Pt-100	Temperature	Thermoresistive metal: T ® r	Resistor
Amperometric sensor	Concentration	Electrochemical reaction: conc. ® I(V)	I-curve generator
Interdigitated finger electrode	Conductivity	Finger - structure: s_{ions} ® $i_{electrons}$	Impedance

Now the structure of this report becomes clear. The second, third and fourth column of this table can be the guidelines for a structural classification of sensor principles.
First, in chapter 3, the available sensors will be categorized on their receptor parts. This is interpreted here as a list based on the used materials. It is started with cheap, single strip, sensors and goes to complicated sensors with diffusion areas and ion exchange membranes.
In chapter 4 some parameters are chosen that might be of interest for washing processes and a list is given of the most common methods to measure these parameters. So this is based on the second column of the table.
The fourth column is the base for chapter 5 where known passive and active electronic devices are listed with their parameters. A summary is given on what chemical and physical influences do modify these device parameters.

2. Measurement technologies

Generally, a sensor should give an output signal as function of an input signal, related by a certain sensitivity parameter. If a linear relation is assumed, two things are important: the slope of this relation and the intercept at zero input (figure 2.1).

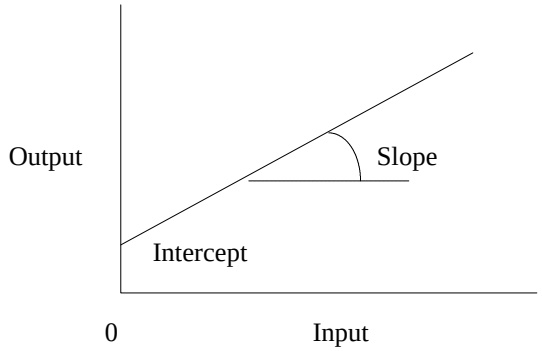


Fig. 2.1: Simplistic representation of a transducing mechanism

The operational model of a device gives the operator information about the input when the output is measured. This requires a characterization of the slope and the y-intercept, either by calibration or complete determination of the model. When according to the model a guaranteed zero output is observed at zero input, a one point calibration will be sufficient, else at least a two point calibration must be performed.
The origin of a non zero y-intercept comes from the fact that the reference is often not well defined. The dependency on accurate references and calibration are the key problems in sensor applications.
In the following subsections some sensor principles are being considered from the calibration and reference point of view.

2.1. Self generating vs. modulating

If a sensor is seen as a transducer of energy from one domain to another, two types can be distinguished. The first are sensors which convert energy from one domain to another. As a result, the output signal will be zero when no input is present and the only energy applied is the energy of the signal itself. This is called a self-generating transducer [4] and an example is the thermocouple.
The second group of transducers are devices to which energy is applied by a source and modulated by a physical or chemical parameter. This are modulating transducers and examples are the ISFET and the Pt-100.
Because self generating transducers have no output signal at zero input is present, there will be no intercept and only the slope must be known (calibrated).

2.2. Differential measurements

With modulating transducers, the y-intercept (specific output at zero input) can sometimes be eliminated by taking the relation to another element which is not sensitive to the measured parameter. Zero output means that the conditions at the measuring device are equal to that of the other device. This is a relative measurement with which common undesired signals can be eliminated.
An often used differential set-up is the Wheatstone-bridge (Fig. 2.2).

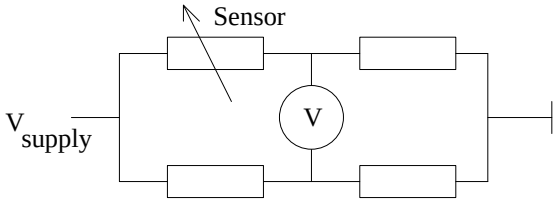


Fig. 2.2: The Wheatstone bridge

The advantage of bridge set-ups is that the output voltage V can be set to zero at a desired sensor output and that common signals on the branches are being eliminated.

2.3. Calibration by finding an absolute value

The coulometric sensor/actuator device uses a special principle [5]. Two ISFETs are differentially measured where one is modulated with locally generated protons. The sensed parameter is the end-time of a titration curve, which is the time necessary to reach the point where the pH has an abrupt change. The measurement of the end point from the non-linear response results in an elimination of the demands on a potential reference.

2.4. Dynamic measurements

The technique described in the previous subsection is a dynamic measurement. In a dynamic measurement, generally a known input is related with the parameter to be measured in a stimulus-response approach.
The most simple form of an actuator/sensor system is a technique called "known addition". This technique will be explained here in terms of pH determination but it can be used to measure a lot more. When a non-bufferred sample has an unknown H^+ concentration C_{sam}, and a volume with a standard H^+ concentration C_{std} is added, then the difference between the pH before and after addition results in:

$$pH_{before} = -\log(C_{sam})$$
$$pH_{after} = -\log\left(\frac{C_{sam} + p \cdot C_{std}}{1+p}\right)$$

where p is the ratio standard/sample volume. The sample concentration can now be calculated:

$$C_{sam} = \frac{p}{(1+p)10^{-\Delta pH} - 1} \cdot C_{std} \qquad (2.1)$$

Instead of measuring an absolute value, now a difference is being measured. This has the advantage that problems with drifting offsets are eliminated. The problem however is, that the accuracy is now dependent on the accuracy of the actuator.

In chrono amperometric measurements, the response on an applied potential step has a linear relation to the inverse of the root of the time. This linear relation can be used by only taking the slope (instead of absolute values) from which information about concentrations can be determined [6].
A dynamic measurement application of an ISFET is the ion-step technique [5] where a non-equilibrium situation is accomplished by changing the ion concentration in a flow system.

3. Sensor classification by technology

In this section a comparison is made between technologies applied to produce the sensors. The summary is made with only thin film technology in mind, but thick film methods can be used as well.
First the cheapest option is chosen. This is the case in which only deposition and patterning is allowed, while also spinning and other casting methods of for instance polymeric layers are possible. After that an overview is given of what is possible if diffusion areas are allowed. This will lead to more complex devices.
In the summary, the material of interest is mentioned first. After that the possible modes of operation are given. Applying simultaneously or sequentially different operational modes is the key to integrating functions on one structure. In many cases, operational modes are created by forcing a current through another part of the structure, for example through the solid parts of the structure or from the structure to an electrolyte.
Besides using different operational modes of a single structure, improvement can be obtained by interpreting the output signals of two or more sensors. Both techniques attempt to get an image of a chemical or physical process by means of polygraphy.

3.1. Patterning and evaporation only

First assume that only deposition and patterning of materials is allowed. The technology can be either thin film (silicon technology), print screening, thick film or macro technology (for example metal electrodes). Available materials are summarized in table 3.1.

Table 3.1: Materials that can be applied using deposition and patterning

Material	**Examples**	**Deposition**	**Patterning**
Metal	Al, Au, Pt, Cu, ...	Evaporation, sputtering	Lift off, wet or dry etching
Semiconductors	Si, group III-V and II-VI compounds	CVD Polysilicon	Wet etching or RIE
Oxides	Ta_2O_5, IrOx, SiO_2, ...	Direct sputtering or evaporation (sputtering) with a subsequent oxidation,	Patterning of metal before oxidation, several etching techniques
Polymers	PVC, Polysiloxane	Spinning, dipping or electrochemical deposition	Photolithography after adding photo initiator, photopolymerisation

3.1.1. Making use of metal films

Methods that do not result in chemical modifications of metal and electrolyte

First the methods are listed that can be performed using metal films, with the aim of avoiding electrochemical modifications of both the metal and the electrolyte in order to get information from physical properties.

a) Current through a metal strip

Set-up: Single metal strip
Applied signal: Voltage or current
Measured: Current or voltage
Frequency: Low
Information: Sensing of temperature or heat actuator

The resistivity of a conducting strip is dependent on the temperature. An example is the Pt-100 element [7]. The Pt-100 uses the thermoresistive effect of a platinum strip of 100W. Such a strip has a nearly proportional resistive behaviour over a moderate range of temperature, the resistance can be written as:

$$R_T = R_0[1 + \alpha(T - T_0)] \qquad (3.1)$$

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.

The inverse of the previous described thermoresistive effect is also possible. When a current flows through a resistance, energy is lost in the form of heat. So a current flow through a metal strip can be used either to sense or to change the temperature.
Applications of the heat actuator can be found in combination with the temperature sensor. Generally some heat is produced and the temperature is measured elsewhere. Examples are specific heat capacitance (with gasses), time-of-flight flow measurements and anemometry. These techniques will be described in a subsequent chapter.

b) Current between metal electrodes through a liquid

Set-up: Two contacts, usually interdigitated finger structure
Applied signal: Sine current or voltage
Measured: Voltage or current
Frequency: Moderate (1-100kHz)
Information: Conductance of electrolyte

Now an AC current is forced from a metal strip, through a test solution, to a second metal strip. This experiment gives information about the conductivity of the test solution. An example is the interdigitated finger structure (two points conductivity set-up). The problem with this device is that the unknown and varying electrode interface potential is part of the current loop, so this gives an error in the measured conductance. Improvements are the four points set-up and the use of capacitive probes (following subsections).

A modification can be that the current is not forced through an electrolyte, but through a selective membrane which is placed on the sensor. Changes in the membrane conductance as a function of some specific reactions from species of the bulk with the membrane are being sensed then.

c) Electrolyte potential sensing

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

An AC current is forced through a test solution using two electrodes, which will have unknown electrode interface potentials. The sensing of the induced potential in the liquid, however, is done using two inner electrodes. Now the measured potential is in a circuit with zero current and no interfacepotential is registered. This is an improvement of the previous described one.

d) 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: Electrical double layer capacitance

With the charge step method a fast current pulse is applied to the cell and the open circuit potential is recorded as a function of time. The current-pulse length is chosen to be sufficiently short that it only causes charging of the electrical double layer. This method has some advantages in the study of electrodes because only non-faradaic processes are selected [8] and the electrical double layer capacitance can be determined.

e) Shottky diode operation

Set-up: Group VIII metal (Pd, Ni or Pt) on silicon substrate
Information: Hydrogen gas concentration

Although in theory an undoped silicon substrate with a metal layer is a Shottky diode, in practice only doped silicon will be used in diodes. The chemical sensitive Shottky diode will be discussed in the section with doped regions.

Methods that result in chemical modifications of metal and electrolyte
1. Controlled potential techniques

In principle, electrochemical experiments can be performed using two electrodes in a liquid. The reactions will take place at both electrode-liquid interfaces and both will be visible in the measured current. To monitor the behaviour of a single 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 when this is possible.

f) Chrono-amperometry

Set-up: Two electrodes or potentiostat (three electrodes)
Applied signal: Single potential step
Measured: Current in time
Frequency: Moderate (after steep step)
Information: Concentrations, Faradaic and non-Faradaic information, diffusion coefficients

After applying a negative potential-step to a working electrode (larger than the standard electrode potential) the electrochemical equilibrium

$$\mathrm{Red} \leftrightarrow \mathrm{Ox} + e^- \qquad (3.2)$$

moves to the left. 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 at the electrode surface, the current is described by the Cottrell equation [8]:

$$i(t) = nFAC_{Ox}\sqrt{\frac{D_{Ox}}{\pi t}} \qquad (3.3)$$

with n the number of electrons transferred per reduced molecule or ion, F the Faraday constant (9.64867×10^4 C/mole), A the interface surface, C the bulk concentration and D the diffusion constant. This equation shows that from an i(t) versus $1/\sqrt{t}$ curve the concentration of Ox can be found when the diffusion coefficient is known. Because this is a slope method, the absolute value of the current is not important, and the reference electrode (as being used in a three electrode system) might be omitted, resulting in a two electrode system. This can only be done when the potential step size across the working electrode/electrolyte interface is known.
Models are present for cases without complete depletion at the electrode surface as well [8].

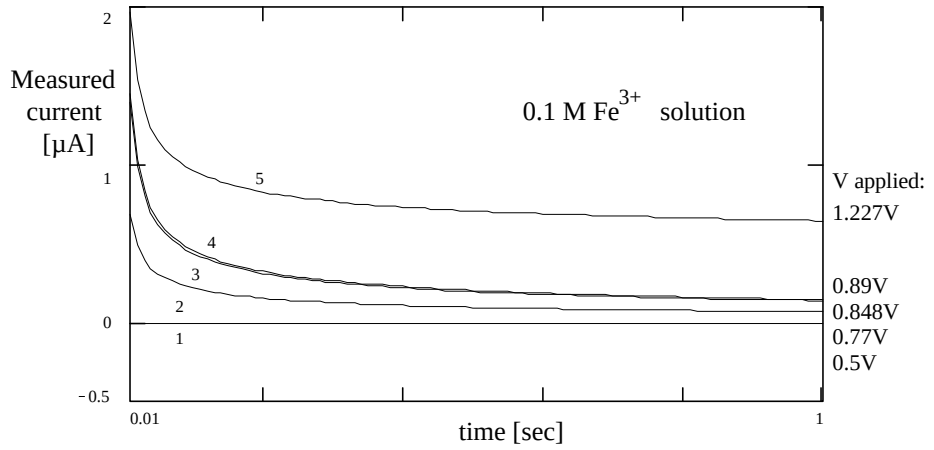


Fig. 3.1: Calculated example of chronoamperometric experiment

Just after the steep potential step, the surface double layer is being charged. This gives a fast exponential current response called the non-Faradaic charging (see section 3.1.1.d). Secondly the diffusion limited Faradaic processes become more important.
In figure 3.1 a calculated drawing of a chronoamperometric experiment is shown. Five different potential steps are evaluated. In curve 1 the potential step was lower than the standard electrode potential necessary to reduce the present ions and no current is bserved. Curve 2 is the result of a redox reaction where the electrode surface is not completely depleted from reducing species. Curves 3 and 4 are the most interesting: now immediate depletion of the electrode surface appears and the response is independent of the step size according to the Cottrell equation. While curves 1 to 4 will go to zero after some time, after the fifth step a net current remains because of the reduction of water.

g) 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 steep steps
Information: Concentrations, E^0 values

Here a large number of chrono-amperometric experiments are performed with increasing potential step size, the current is sampled after time t. A graph is made of the sampled current versus the step size.

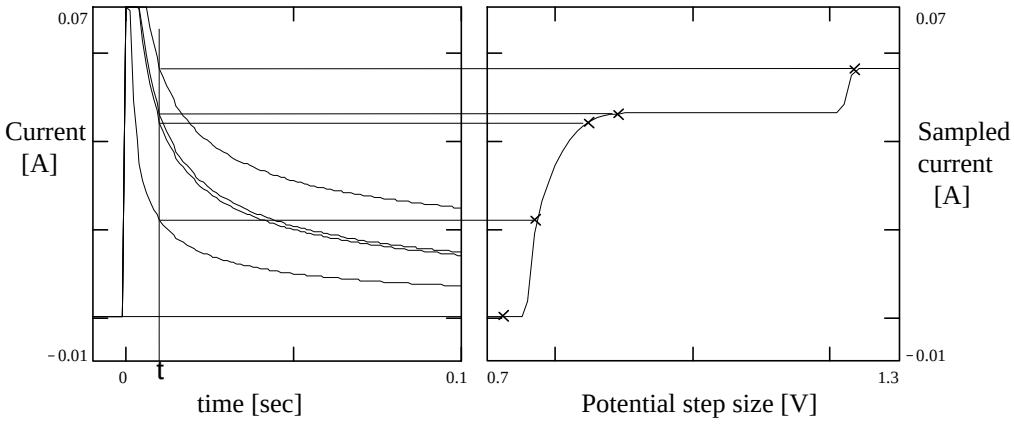


Fig. 3.2: Schematic drawing of sampled current voltammogram

The advantage in relation to chrono-amperometry is that besides the determination of concentrations, E^0 values can be found as well. This technique is the base of polarography, which requires a more complex set-up when peformed using a dropping mercury electrode [9].

h) 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 steep step
Information: Concentrations, Faradaic and non-Faradaic information

The aim is to restore depletion of species made by a potential step by doing a subsequent reversal potential step. This is called a reversal technique.

i) Polarographic methods

Set-up: Dropping mercury electrode in potentiostat set-up or Pt -electrode
Applied signal: AC, DC or pulsed potential
Information: Finger-print of all reducing (or oxidising) species

A polarogram gives a graph with the applied potential on the horizontal axis and the measured current on the vertical axis. The result resembles sampled current voltammetry, but now the graph is measured directly. The reaction mechanisms involved are diffusion controlled. Models for AC-, DC-, pulsed- and other polarographic methods are well developed [8].

With a DME (Dropping Mercury Electrode) it is possible to do a number of polarographic experiments. The DME refreshes continually it's surface, and due to the set-up the relative contribution of charging currents is reduced.

The pO_2 electrode [1] is an example of a polarographic sensor. Here oxygen and water are reduced to hydroxide ions. Selectivity is obtained by shielding the platinum electrode with a gas permeable membrane (teflon). The corresponding polarogram shows a potential range were the measured current remains constant, the saturation area, which is the result of a diffusion controlled current. A higher partial oxygen pressure results in a higher saturation current.

j) Coulometry

Set-up: One of the amperometric types
Information: Amount of substance electrolyzed

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

$$Q(\tau) = \int_{t=0}^{t=\tau} Idt \, . \qquad (3.4)$$

The information from a coulometric experiment is the amount of reduced species.

k) Potential sweep methods

Set-up: Two electrodes or potentiostat (three electrodes)
Applied signal: Potential triangle
Measured: Current in time
Frequency: Low, typical slopes are in the range of 1 - 100 mV/sec
Information: Concentrations, Reaction mechanisms

The most common version is Cyclic Voltammetry. With these methods a fingerprint of the electrolyte is obtained by scanning a range of potentials and coming back to the first one.

Figure 3.3 shows a characteristic cyclic voltammogram for a reversible reaction of one species.

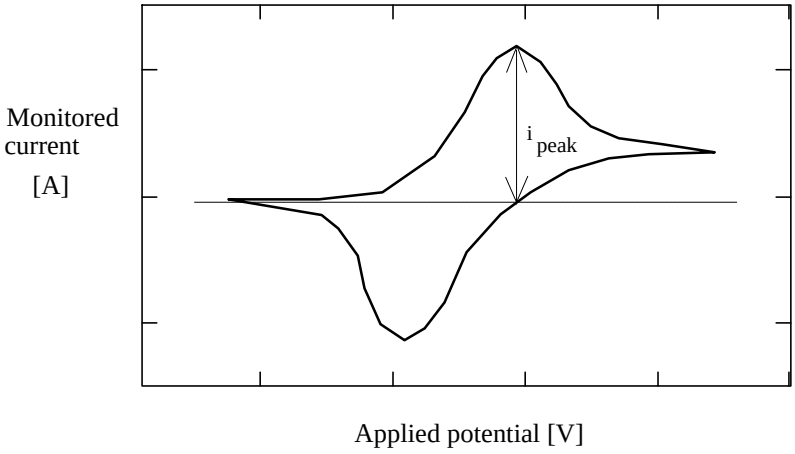


Fig. 3.3: Schematic drawing a cyclic voltammogram

Models for cyclic voltrammograms can be found in literature [8], for example the peak current will be:

$$i_{peak} = (2.69 \times 10^5) n A C_0 \sqrt{n D_0 v} \qquad (3.5)$$

with n the electrons involved, A the electrode surface, C_0 the bulk concentration of the species responsible for the peak, D_0 its diffusion constant and v the scan rate. The dependency on the scan rate is characteristic for cyclic voltammograms.

The relation between some controlled potential techniques can be explained with figure 3.4, which shows a range of chronoamperometric experiments in one three-dimensional graph.

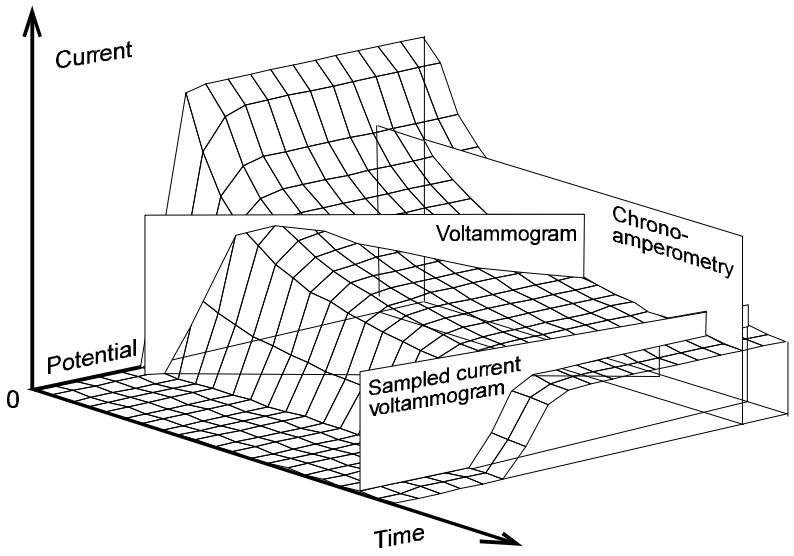


Fig. 3.4: Some controlled potential techniques in one i(v,t)-graph

The graph is made using a number of chrono-amperometric experiments with step sizes ranging from zero to a certain positive potential. A sampled current voltammogram can be constructed by taking the currents after time t. One branch of a cyclic voltammogram is the curve in a plane where both the potential and time are varied.

Methods that result in chemical modifications of metal and electrolyte
2. Controlled current techniques

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 [8]. Usually the mathematics involved in solving the diffusion equations are much simpler as well.

l) (Constant current) chrono potentiometry

Set-up:	Two electrodes or potentiostat
Applied signal:	Current step
Measured:	Potential
Frequency:	High, steep step
Information:	Determination of concentrations

After applying a constant current to a metal electrode, the electroactive species in the electrolyte will be reduced or oxidised, depending on the direction of the current. 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.

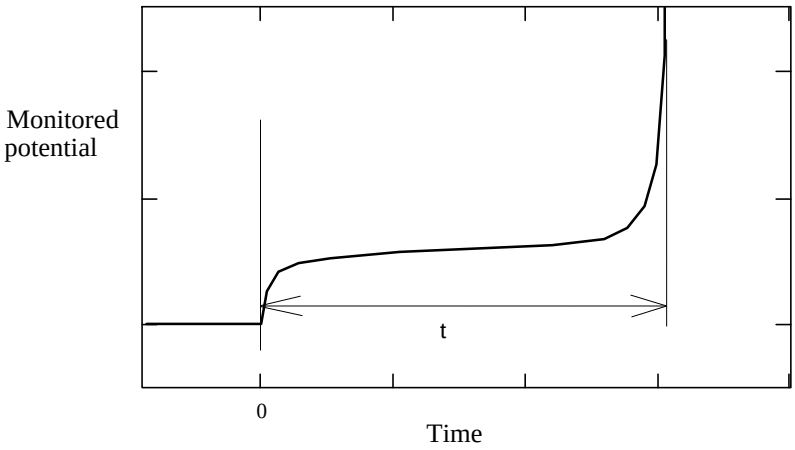


Fig. 3.5: Chrono potentiometry and the transition time t

The time to reach depletion is called the transition time and is proportional to the diffusion constant and the square of the concentration. This transition time is described by the Sand equation [8]:

$$\tau = \frac{\pi D_{Ox} n^2 F^2 A^2 C_{Ox}^2}{4 i^2} \qquad (3.6)$$

where the parameters have the same meaning as in the Cottrell equation (3.3) except for the current i which is now the applied current.

Set-up: Working electrode and counter electrode
Applied signal: Current
Frequency: Low, DC
Information: Adaptation of the local H^+ or OH^- concentration, for example

Besides this potentiometric sensor function, an actuator operation can be performed as well. By applying a current, the local electrochemical generation of H^+ or OH^- from water can be controlled:

$$2H_2O + 2e^- \rightarrow H_2 + 2OH^- \qquad (3.7)$$

$$2H_2O \leftrightarrow O_2(g) + 4H^+ + 4e^- \qquad (3.8)$$

dependent on the direction of the current.
An application is the coulometric sensor-actuator device were the pH control is used to perform a coulometric acid-base titration, being sensed by ISFETs.

Set-up: Working (cavity) electrode and counter electrode
Applied signal: Current
Measured: Overpotential or impedance
Frequency: Low
Information: Dynamic surface tension, surfactant concentration

The generation of hydrogen gas can be used for a second actuator function. The development of a dynamic surface tension (DST) sensor is currently performed (Alex Volanschi [10]). This device consists of a current controlled working electrode which generates hydrogen gas bubbles. From the fluctuations in either the electrode impedance or the over potential the bubble frequency can be determined. It appeares that this frequency is proportional to the surfactant concentration.
Actually this device is not a simple metal film. To control gas nucleation an anisotropic etched area is being used.
The problem with this type of measurement is that the operational model is not yet completely described, the bubble-frequency/surfactant-concentration relation is surfactant-type dependent so a calibration curve is needed.

m) Programmed current chrono potentiometry

Set-up: Two electrodes or potentiostat
Applied signal: Programmed current function
Measured: Potential
Frequency: Low
Information: Concentrations, Faradaic information

Rather than a constant current, a current that varies as a known function of time can be employed. The most common is the current ramp, but this procedure is reported only rarely.

n) Current reversal and cyclic chrono-potentiometry

Set-up: Two or three electrodes
Applied signal: Current step
Measured: Potential
Frequency: High, steep 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. The advantage is that the starting final situation of the experiment is equal to the initial state.

o) 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.
An effective discrimination between Faradaic and non-Faradaic properties is possible.

p) 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. Besides that, very low concentrations can be detected because of the concentrator effect.

3.1.2. Making use of semiconductors

In this subsection, the combination of semiconducting materials and metal layers is being considered. Semiconductors that are reported mostly are:

- Ge and Si (group IV elements);
- GaAs (III-V compound);
- CdS and ZnO (II-VI compounds);
- TiO_2 and SnO_2 (III-VI compounds).

The compounds are more used in discrete sensors because germanium and silicon have a very sensitive behaviour towards impurities.

a) Current through a semiconductor

Set-up: Resistor built of semiconductor material, thermistor operation
Measured: Resistance
Frequency: Low
Information: Temperature

The conductivity of semiconductors changes with temperature. For silicon this dependency is approximately eight percent per degree. This temperature dependency places a limitation on the use of semiconductor devices in some circuits. On the other hand, for some applications this property of semiconductors is used as an advantage.

Semiconductors used in this manner are the thermistor and the spreading resistance temperature sensor.
Silicon and germanium are not used as commercial thermistors because their properties are too sensitive to impurities. Sintered mixtures of NiO, Mn_2O_3 and Co_2O_3 are used. The resistivity changes exponentially with temperature.

Set-up: Resistor build of semiconductor material, strain gauge
Measured: Resistance
Frequency: Low
Information: Force, bending

The resistivity of some semiconductors is dependent on the strain in the material: this is the piezo-resistive effect. Strain gauges are generally based on slices of semiconducting material.

b) Piezo electric operation

Set-up: Material as dielectric material
Applied signal: Mechanical input
Measured: Potential
Information: Mechanical pressure/ force

Some semiconductor compounds show piezo electric behaviour. This phenomenon can be used in piezo crystals and pressure sensors. Piezo crystals are being used in mass sensors as SAW (surface acoustic wave) devices to measure the mass of deposited materials.

c) Using electrical interaction with an electrolyte

Set-up: Semiconductor in contact with an electrolyte
Information: Gas concentration (TiO_2-gas sensor)

This section is about patterned films only, so the semiconductors mentioned here are intrinsic ones (doped semiconductors will be evaluated in the part of this report were diffusion areas are allowed).
The electron transfer across a semiconductor/liquid interface can easily be understood by looking at the energy levels [11]. 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 [12] similar to the situation that will be described in subsection

3.1.3. about insulating oxides (actually, many semiconductors will form an oxide layer at their surfaces).
In literature only a small number of applications of semiconductor/liquid interfaces are reported. A solid state sensor based on a bare semiconductor/liquid interface is the SnO_2 gas sensor [4] which has a dissolved gas dependent resistivity.

3.1.3. Making use of oxides

Oxides cover a wide variety of materials with also a wide range of properties. In this list, the oxides are grouped as conducting and insulating types. Some oxides that show semiconducting properties were mentioned in subsection 3.1.2. Most sensor applications based on oxides make use of metal layers, so the oxide-technology must be seen as an addition to the metal layer technology.

a) Using insulating oxides for capacitive sensing

Set-up: Sandwich of conductor/oxide/electrolyte
Applied signal: AC-Voltage
Measured: AC-Current
Frequency: Moderate
Information: Conductance

Whereas with conductor/liquid interfaces the potential drop is mainly across the Helmholtz layer, in insulator/liquid interfaces a significant potential difference exists across the insulator. Because of the insulating layer only capacitive measurements, like conductivity measurements [13], can be performed.

Semiconductor oxides generally 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 surface 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 specific redox processes is reduced.
An application is the conductivity sensor [13] using this special oxide in a two points electrolyte conductance measurement. In this case a two point set-up is possible because of the low impedance of the oxide/solution interface.

b) Using conducting oxides

The resistivity of some metal oxides (like SnO_2 and TiO_2) depends on temperature and dissolved gases [4]. The tin-oxide CO gas sensor is a standard one and was mentioned earlier as an application of a semiconductor/electrolyte interface.

Ruthenium oxide (RuO_2) electrodes have an extremely low overpotential for hydrogen evolution and are used for the production of Cl_2 gas and in fuel cells [14].

Generally, conducting oxides can transport ions besides electrons. They are sometimes referred to as mixed conductors. The electrochemical properties of conducting oxide-films are completely different from metal films and insulating oxides.

The most common conducting oxide is iridium oxide. In theory, 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. An application is the controlled injection of protons from the IrOx film into the electrolyte (coulometry).

Thin film metal oxides have been investigated for use as pH electrodes. A number of oxides is being tested including PdO, RuO_2, PtO_2, TiO_2, OsO_2, IrO_2, RhO_2, Ta_2O_5 and SnO_2. IrO_2 and RuO_2 were the most promising materials [15]. With these materials a potentiometric pH sensor can be realized. The use of iridium oxide in various oxidation states appeared to give a pH sensitivity dependent on this oxidation state [16].

3.1.4. Making use of polymers

The application of polymer membranes offers a lot of advantages for sensor technology. They are relatively low cost materials and their fabrication techniques are quite simple (non-cleanroom processes) [17]. They can be placed on either monolithic semiconductors, ceramics and glasses or thick and thin film devices.
Most conventional ion selective electrodes (ISEs) contain a polymer membrane.

a) Using dielectric properties
Set-up: Membrane as dielectric material in a capacitor
Measured: Polarization
Information: Mechanical influences, moisture
After applying a bias potential to some polymers, polarization occures. This polarization can be changed by either mechanical stress or temperature (piezo-electric respectively pyro-electric effects). These materials have a wide application in the field of pressure, acceleration, and acoustic sensors.
Dielectrics which can hold an applied polarization for a long time (electrets) can be used in capacitive acoustic sensors. The change in permittivity can be used for humidity sensing.

b) Using polymers as an ion exchange medium
Set-up: Membrane on either finger structure or ISFET
Measured: Nernstian interface potential
Information: Concentrations
Polymers like PolyVinylChloride (PVC) and polysiloxane are permeable to ions and gasses, so those polymers can be considered as being solid electrolytes. The liquid to polymer interface will be between two ionic conductors. Some other not-polymeric materials like ZrO_2 and LaF_3 show a similar behaviour [12]. The advantage of these materials lies in the possibility to make ion sensitive electrodes (ISE's) in a very simple way.

As an example the fabrication of an ion selective PVC membrane is mentioned here. The polymerisation is done from a cocktail containing the following contaminants:
a Solvent: Tetrahydrofuran (THF);
b Membrane matrix: PolyVinylChloride (PVC);
c Plasticizer;
d Ionophore;
e Additive: SodiumTetraPhenylBorate (NaTPB).
After evaporation of the solvent the membrane consists of a solid matrix holding the ionophore and the additive.
Ionophores are ion selective molecules, the additive is present to permselect the membrane in order to prefer anions or cations. The proper operation of the membrane is based on the buffering behaviour of the additive/ionophore combination.

Detection of the primary-ion dependent behaviour of such membranes can be done by placing the membrane on an ISFET (the ChemFET).

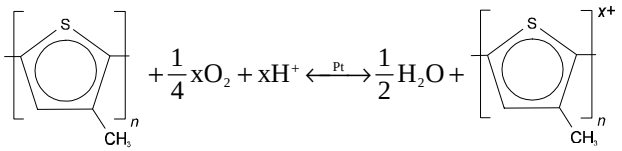
c) Using polymers for electrical conductance measurements

Set-up: Membrane in contact with electrolyte, placed on a conductivity sensor
Measured: Conductance of membrane
Information: Concentrations

The functioning of membranes used for Nernstian potential based sensors (mentioned above) is based on a system which buffers the primary ion concentration in the membrane. Only then, the boundary potential changes Nernstian (59 mV/dec) with the concentration of primary ions in the electrolyte. The opposite case is obtained when the primary ion concentration changes with the primary ion concentration in the electrolyte. In that case, the conductivity of the membrane gives an impression of the primary ion concentration in the electrolyte.

Set-up: Membrane in contact with electrolyte
Measured: Conductance of membrane
Information: Concentrations, oxidizing or reducing state

By impregnating conducting polymers with a metal, the membrane becomes responsive to oxidizing and reducing species in an aqueous environment.
An example is poly(3-methylthiophene) with metallic Pt [18], or other noble metals. The advantage of poly(3-methylthiophene) is that it is conducting when oxidized (after O_2 exposure) and insulating when reduced (after H_2 exposure). Under aerobe conditions, 1 atm O_2 for example, the device is conducting at low pH and insulating at high pH.
The assumed equilibrium involved is:



(3.9)

Polypyrrole [19] shows another behaviour, it can be used to form membranes with electrically switchable ionic permeability. The ionic permeability is switched by control of the polypyrrole oxidation state with a potential applied to a membrane embedded gold electrode [20].

3.1.5. Making use of anorganic selective membranes

Glass (as used for the pH glass electrode) is not the only electrode material capable of a selective Nernstian response to specific ions. Table 3.2 gives a summary of some important electrode materials [7]. The ion selective electrodes (ISEs) obtained are often used as potentiometric sensors.
A class of anorganic selective materials are the chalcogenide glasses [28]. This are membrane materials (mainly Ag, S, and As alloys) that are highly ionic conductive . They are used for the determination of heavy metal cations (Ag^+, Cu^{2+}, Pb^{2+}, Cd^{2+} and Fe^{3+}), iodide and bromide.

Table 3.2: Some solid-state anorganic membrane electrodes

Ion	Ion-exchange medium	Operating rages [M]	pH range	Interferences and selectivity
Ag^+	AgS crystal	$1 - 10^{-7}$	0 - 14	No significants
Br^-	AgBr crystal	$1 - 5\times10^{-6}$	0 - 14	$Cl^- = 2.5\times10^{-3}$ $I^- = 5\times10^{3}$ $CN^- = 1.2\times10^{4}$ $OH^- = 3\times10^{-5}$ $NH_3^- = 0.5$
Cl^-	Silverchloride (polycrystalline)	$1 - 5\times10^{-5}$	0 - 13-pCl	$Br^- = 300$ $I^- = 2\times10^{6}$ $CN^- = 5\times10^{6}$ $OH^- = 0.012$ $NH_3^- = 8$ S^{2-} must be absent
Cu^{2+}	CuS-Ag_2S mixture	$1 - 10^{-5}$	0 - 14	Ag, Hg must be absent High levels of Cl^- and Br^- will form complexes $Fe^{3+} = 10$
F^-	LaF_3 single crystal	$1 - 10^{-6}$	0 - 12-pF	$Br^- = Cl^- = I^-$ $= NO^{3-}$ $HCO_3^- = 10^{-3}$ $OH^- = 0.1$
I^-	AgI crystal	$1 - 5\times10^{-8}$	0 - 14	$Cl^- = 10^{-6}$ $Br^- = 2\times10^{-4}$ $CN^- = 0.4$ $S_2O_3^{2-} = 10^{-5}$ S^{2-} and strong reducing agents must be absent
S^{2-}	AgS crystal	$1 - 10^{-7}$	0 - 14	No significants

3.2. Adding diffusion areas

After the previous section, which gave a summary of possible sensing techniques which can be performed using structures on a silicon substrate, this section gives a summary of possible techniques that can be done with structures on and diffused in the substrate. While in the previous section the realization could be in either thin-film, thick-film or macro electrodes on any substrate, now we are restricted to using silicon technology (thin film transistors, however, can be made on a lot more substrates).
Using diffusion areas, pn-junctions (and so transistors) can be made. This allows a much wider range of sensors, for example a wide variety of ISFET based devices. The most common observed operational modes can be divided in:
- Operation frequency
- Whether an electrical current flows in the substrate only or through the electrolyte

3.2.1. Applications of a single doped region

This is an expansion of the semiconductor/liquid interface mentioned in section 3.1.2. If the semiconductor is doped the application is more convenient because the behaviour is controlled. The semicondcuctor/electrolyte interface behaves like a pn-

junction. By adding more donor or acceptor states, the semiconductor begins to behave more like a metal.

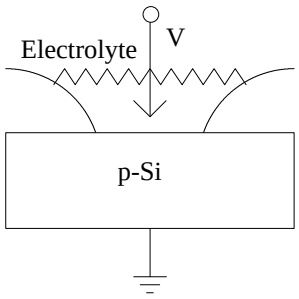


Fig. 3.6: The doped semiconductor-electrolyte device

The relation between current and voltage is given by [21]:

$$I_{\phi_{E=0}} = AT^2 e^{-\frac{q\phi_B}{kT}} \tag{3.10}$$

or

$$I = I_0\left(e^{-\frac{q\left(\phi_1-\phi_1^0\right)}{kT}} - 1\right) \tag{3.11}$$

with I the current density, $If_{E=0}$ the current density at zero electrode potential, A Richardson's constant, T the absolute temperature, f_B the Schottky barrier potential and (f_1-$f_1{}^0$) the voltage across the structure. These formulas do resemble the Shottky behaviour (metal/semiconductor interface).

Applications of doped semiconductors can be found in the capacitive methods like impedance measurements.

3.2.2. Applications of metal-semiconductor contacts

A metal layer on a semiconductor (or a heavily doped semiconductor on a semiconductor) is known as the Shottky barrier diode. Two sensing principles were developed using this Shottky mode.

a) Shottky diode operation

Set-up: Metal on silicon (all currents in solid parts)
Applied signal: Voltage
Measured: Current
Information: Electrical rectifying behaviour, temperature

In this mode no interaction with an electrolyte is assumed. A metal in contact with a doped semiconductor gives a potential-current behaviour like:

$$I = AT^2 e^{-\frac{\psi_B}{kT}}\left(e^{-\frac{qV}{kT}} - 1\right) \qquad (3.12)$$

with I the current density, A the Richardson's constant, T the absolute temperature, y_B the Shottky barrier energy and V the potential across the diode. So just like the normal pn-diode a temperature dependency will be observed.

Set-up: Pd on silicon in contact with an electrolyte
Measured: Rectifying behaviour
Information: H_2 gas concentration

When the metal layer is catalytically active, a gas dependent behaviour is observed. In practice the metal is almost exclusively Pd and the semiconductor ZnO, TiO_2 or CdS.

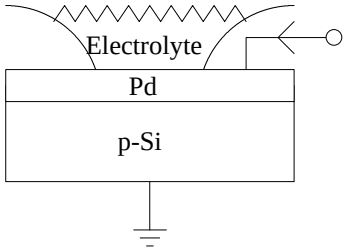


Fig. 3.7: Hydrogen gas sensor using a Pd Shottky diode

The dependency observed is towards dissolved hydrogen gas. Hydrogen molecules in air are dissociated on the Pd surface and some of the atoms diffuse through the thin metal layer. They are adsorbed on the metal-semiconductor interface which results in a change in the Shottky diode properties [22].

3.2.3. Applications of single pn-junctions

Two operational modes were developed using a single pn-junction, one with only currents in the bulk, and one with electrical interaction with an electrolyte.

a) pn-Junction diode operation

Set-up: All currents through single pn-junction
Measured: Electrical rectifying
Information: Temperature

To have pn-junction operation, currents flowing in the device must be forced to stay in the substrate. When this is the case, a temperature measurement can be performed. High doping of one of the regions gives a Shottky behaviour.

b) Current from substrate to the liquid

Set-up: BJT where collector is exchanged by an electrolyte
Information: Separation of valence and conduction band processes

A technique called "transistor technique" is sometimes used to evaluate electrode reactions because valence band electrons and conduction band electrons can be detected separately [11]. 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.

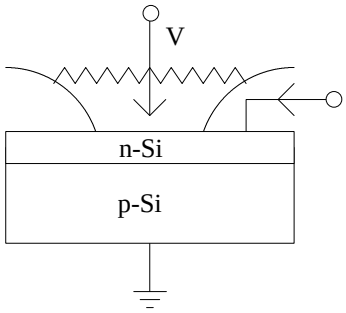


Fig. 3.8: pn-Junction used for the transistor technique

A bipolar junction transistor is formed with the electrolyte as a collector.

3.2.4. Applications of dual pn-junctions

Two pn-junctions together may form a bipolar junction transistor. The structure can be either planar or in the bulk.
From literature no complete bipolar transistors in contact with liquids were reported (structures that look like a bipolar junction transistor were mentioned before as the transistor technique, but they use a single pn-junction).

a) Without contact to an electrolyte, bipolar junction transistor

Set-up: PTAT set-up (a-symmetric current mirror)
Measured: PTAT potential
Information: Temperature

In addition to the single pn-junction temperature sensor, a better temperature sensor is the PTAT (proportional to the absolute temperature) configuration. The PTAT set-up requires four transistors and will be described in chapter 4.

3.2.5. Applications of insulator on silicon structures

Many insulators are not chemically inert, but show an equilibrium with protons and hydroxide ions (in case of SiO_2 and Ta_2O_5). A wide variety of sensors is based on insulator on silicon structures. The physical and chemical properties of insulators in contact with an electrolyte were mentioned in section

3.1.3. in the subsection concerning insulating oxides.

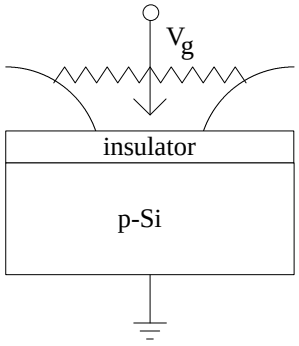


Fig. 3.9: Insulator on silicon structure

To be able to convert a chemical or physical parameter to an electronic signal, some diffusion areas are introduced to get a modulated electronic device. The first operational mode (the ion controlled diode) measures the chemical and physical surface modifications by use of the induced space charge regions in a lateral bipolar junction transistor. The other ones are based on the field effect.

a) Ion controlled diode operation

Set-up: Oxide on silicon np^+n-structure
Measured: Sensing of the depletion region
Information: Concentrations

A practical set-up for a ICD (ion controlled diode) uses a lateral bipolar transistor (figure 3.10) [4]. The size of the depletion regions of the two lateral diodes depends on the interface potential at the ion selective membrane/electrolyte contact.

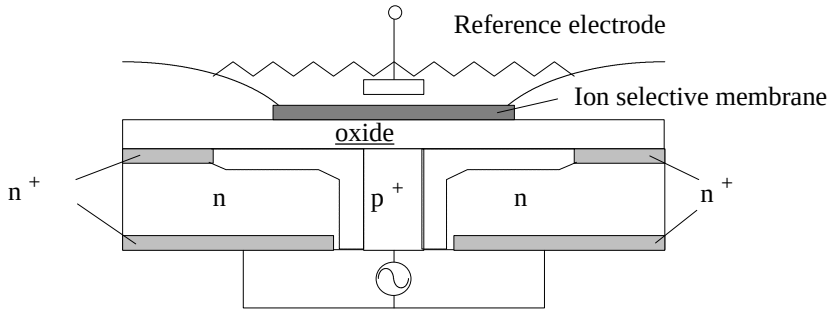


Fig. 3.10: The ICD using a lateral bipolar transistor

By measuring the differential capacitance of the two space charge regions an impression of the ion concentration is obtained [23].

b) Ion sensing with an ISFET structure

Set-up: Standard ISFET
Applied signal: Constant Drain-current and Drain-Source potential
Measured: Threshold voltage
Information: pH

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. The output potential of this amplifier is related to the H^+ concentration.

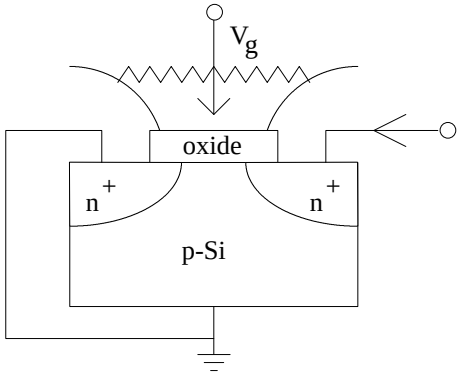


Fig. 3.11: The ISFET

If the insulator is thinner than about 30 nm then tunneling is possible. This would be an ISFET with a tunnable oxide layer. In literature experiments are reported with ISFETs having a gate of 3 nm. They still acted as ISFETs because the tunneling current was low [21].

c) Using membranes on ISFETs

Set-up: ISFET with either organic or inorganic ion selective membrane
Information: Various cations and anions

To make an ISFET selective for other species than H^+ and OH^-, a selective membrane must be added. The first option is to add an organic membrane as mentioned in section 3.1.4. as solid electrolytes. This device is called a ChemFET with which a selective ion detection can be performed.

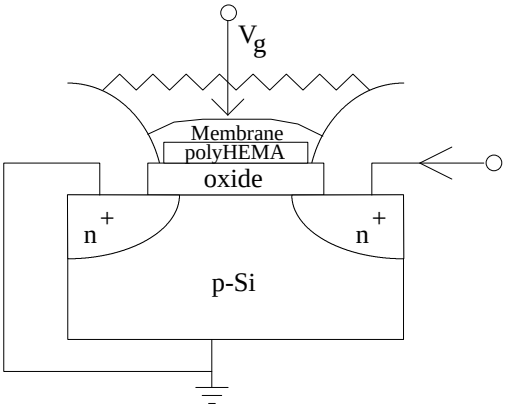


Fig. 3.12: The ChemFET

The polyHEMA later is added to eliminate CO_2 responses and to guarantee a stable interface potential. The membrane-electrolyte interface shows a potential which is Nernstian dependent on the primary-ion activity in the electrolyte.
Ionophores for for example K^+, Na^+, Li^+ Ca^{2+}, Pb^{2+}, Mg^{2+}, NH_4^+ are commercially available.

Anorganic membrane based ISFETs are reported as well, making use of materials mentioned in subsection 3.1.5.

When a ChemFET is taken with a immobilized enzyme membrane, the chemical reactions that are specifically catalysed can be monitored as a pH variation. This is the ENFET.
Other devices (IMFET) have specific immobilized receptors which give a antigen-antibody response. This immuno-reaction can be monitored by the ISFET. Besides that the response can be generated in a bio-active reactor (for instance containing bacteria): The BIOFET.

d) An ISFET structure as a capacitive probe

Set-up:	ISFET
Applied signal:	Electrical current through electrolyte
Measured:	Cut-off frequency (for single ISFET set-up), differential signal (for four-points set-up)
Information:	Conductivity

The cut off frequency in the small signal model of an ISFET is being determined by three physical parts. These are the small signal input capacitance, the cell constant and the electrolyte conductivity (between reference electrode and the ISFET). This last dependency has led to the realization of an ISFET-based conductivity sensor [24]. The measurable conductivity window can be shifted by adapting the geometry of the cell. To get a measurable RC-time the effect of the electrolyte bulk resistance must be reduced by using a configuration with a small window.

With ISFETs in the input stage of a differential amplifier, a potential difference in the liquid can be determined. This can be used in combination with two additional electrodes (metal) which apply a current through the electrolyte. An example is the four points conductivity measurement using two ISFETs [25].

e) Sensor applications of TFTs

Thin film transistors (TFTs) are structures that look like MOSFETs but are completely assembled on top of a substrate which does not necessarily has to be silicon [26]. The basic configuration is drawn in figure 3.13.

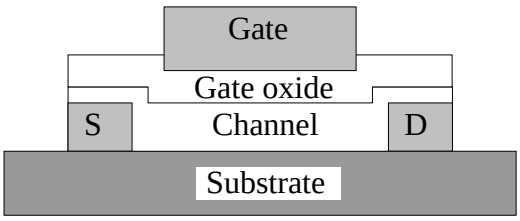


Fig. 3.13: Basic configuration of a thin film transistor

This is the staggered type which can be made in a LPCVD/PECVD reactor without braking the vacuum. The most common semiconducting material is amorphous silicon. Promising results are obtained using silicon-germanium mixtures.
Applications are in the field of active matrix liquid crystal displays and SRAMs. The use of TFTs for Ion Sensing (ISTFTs), catalytic Pd-gate TFTs and light adressable potentiometric sensors (LAPS) has been demonstrated.

3.2.6. Applications of metal-insulator-silicon structures

After having insulators and metals on semiconductors, the combination of metals and insulators on semiconductors is given here. The most commen application is the classical MOSFET. Historically, this device must be placed before the ISFET.

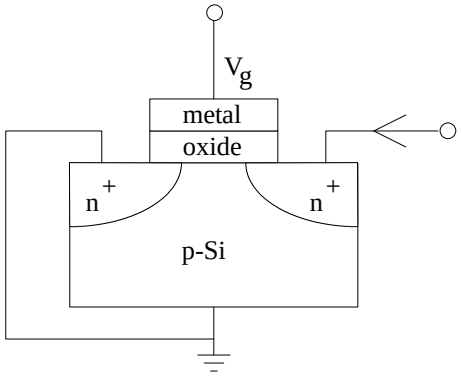


Fig. 3.14: The MOSFET

a) Operation without chemical dependency, the MOSFET
Set-up: MOSFET, no interaction with electrolyte
Measured: A-symmetries in PTAT set-up
Information: Temperature
This is the actual MOS transistor operation. With MOS transistors the same remarks as with the bipolar transistors are valid. An advantage is that the MOS process resembles more like the ISFET process than a bipolar process. Applications in sensing are only in the PTAT set-up. Besides that, transistors in general can be used to make a small on-chip pre-amplifier.

b) Chemical dependent structures
Set-up: MOSFET with chemically active gate material
Information: Concentrations
These structures, sometimes referred to as MISFETs or MIS-capacitors, have a chemical dependent flatband voltage, measurable in their threshold voltage. A sensor is obtained by choosing a chemically active gate material.
Chemical reactivity is known from group VIII elements Ni, Pd and Pt. In this way devices sensitive to hydrogen, carbon monoxide, hydrogen disulphide and ammonia were realized. The behaviour comes from the dipole layer formation at the metal-

insulator interface [22]. The device may be realized with single or multilayered dielectrics.
Other MISFET devices only have a very small layer of insulating material (some nanometers), which is used to prevent undesired formation of intermediate species, while the electrons easily tunnel across this layer.
This device was historically the successor of the chemical sensitive Shottky diode [27] as shown in section 3.2.2. Because the semiconductor materials ZnO and CdS are not very common in the integrated circuit technology, the combination of silicon and palladium was tried for gas sensing. The problem with this device was a formation of an intermediate silicide layer of Pd_2Si. The solution to this problem was the application of a tunnable SiO_2 layer between palladium and silicon.

3.2.7. Summary on structures with diffusion areas

A summary of the mentioned doped-region structures is given in table 3.3. The most solid state applications are based on the electrolyte-insulator-silicon (ISFET) and metal-insulator-silicon (MOSFET).

Table 3.3: Structures using diffusion areas and thin film deposition

Structure	**Examples**	**Modes**
Doped region	Impedance measurement	current from silicon to liquid
Metal-silicon contact	Shottky diode, H_2-electrode	currents in the substrate only, gas sensitive metal layer
Single pn-junction	Temperature, transistor technique	current in diode only, current to liquid
Dual pn-junctions	Bipolar junction transistor, PTAT, on chip electronics	no chem. interaction with liquid
Insulator-silicon structure	Ion controlled diode, tunneling diode, ion sensing ISFET capacitive probe ISFET	thick insulator, thin insulator, "normal" ISFET mode, AC mode
Membrane-insulator-silicon structure	ChemFET	Interaction with liquid
Metal-insulator-silicon structure	MOSFET, PTAT, H_2 sensor	No chem. interaction with liquid, Interaction with liquid

A nice overview based of chemically sensitive semiconductor devices was given by Saaman and Bergveld [21]. This two dimensional graph contains the same information as table 3.3, but now along an "insulator thickness" axis and an "in contact with" axis.

Table 3.4: Structural overview of insulator on silicon sensors [21]

Insulator thickness:	*In contact with:* metal (Physical sensors)	electrolyte (Chemical sensors)
none	**metal-semiconductor** Shottky diode hydrogen gas-sensor	**electrolyte-semiconductor** TiO_2- cel pH sensitive

thin (<30 nm)	**metal-insulator-semiconductor** tunnel diode hydrogen gas	**electrolyte-insulator-semic.** pH sensitive
thick	**metal-insulator-semiconductor** MISFET hydrogen gas	**electrolyte-insulator-semic.** ISFET pH sensitive

3.3. Summary

In the previous sections techniques, operational 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
operational mode.

Table 3.5: Film-only techniques versus diffusion-area techniques

Patterning and evaporation only	**Adding diffusion areas**
Metal films *Methods that do not result in chemical modifications of metal and electrolyte* a) Current through a metal strip b) Current between metal electrodes through a liquid c) Electrolyte potential sensing d) Charge step method (coulostatic impulse) e) Shottky diode operation *Controlled potential techniques* f) Chrono-amperometry g) Sampled-current voltammetry h) Double potential step chrono-amperometry i) Polarographic methods j) Coulometry k) Potential sweep methods *Controlled potential techniques* l) (Constant current) chrono potentiometry m) Programmed current chrono potentiometry n) Current reversal and cyclic chrono-potentiometry o) Faradaic Impedance methods p) Stripping methods Semiconductors a) Current through a semiconductor b) Piezo electric operation c) Using electrical interaction with an electrolyte Oxides a) Using thick insulating oxides for potential sensing b) Using conducting oxides Polymers a) Using dielectric properties b) Using polymers as an ion exchange medium c) Using polymers for electrical conductance measurements Anorganic selective membranes	Single doped region Metal-semiconductor contacts a) Shottky diode operation Single pn-junctions a) pn-Junction diode operation b) Current from substrate to the liquid Dual pn-junctions a) Without contact to an electrolyte, bipolar junction transistor Insulator on silicon structures a) Ion controlled diode operation b) Ion sensing with an ISFET structure c) Using membranes on ISFETs d) An ISFET structure as a capacitive probe e) Sensor applications of TFTs Metal-insulator-silicon structures a) Operation without chemical dependency, the MOSFET b) Chemical dependent structures

4. Sensor classification by measured parameter

In this chapter, a second systematical categorizing of known sensor structures is performed. This categorizing is done with respect to the measured parameter. First, some parameters will be chosen that might be of interest for washing processes.

4.1. Chosing the parameters

To make a decision about the sensors that are needed for monitoring washing processes, table 4.1 gives an impression of desired washing parameters.

Table 4.1: Washing parameters before and during a washing process

Before washing	Type of fabric	The type of fabric (wool, cotton, etc.) present in the tub is hard to determine. Probably this can be left to the operator.
	Color of fabric	In general, two types of wash are being performed: white wash and coloured wash. Because the difference is very hard to measure, this will be left to the operator.
	Load weight	The torque on the motor that rotates the tub gives information about the load weight.
	Amount of soil	An impression can be obtained by evaluating pH and conductivity. For a more accurate measurement, specific sensors for soil contaminants will be needed.
	Type of soil	Specific sensors for detecting bleachable, fatty and stain-like soils.
	Water quality	Hardness, conductivity.
During washing	Water level	An explicit water-level indicator will not be necessary when a torque sensor is present (for the load weight). The mass of the tub will be dependent on the amount of water in the tub.
	Temperature	For control of the temperature a sensor will be needed.
	Detergent effectiveness	Surfactant level, enzyme activity, bleach activity, pH and hardness (builder dosage).
	Rinsing effectiveness, turbidity	For rinsing effectiveness, a secondary parameter must be found which is an indication for the water quality and turbidity. Conductivity and pH might be good indicators because optical methods are assumed as less interesting here.

Terms like water quality, machine load, etc. can not be determined from sensors directly. So from this set of washing parameters, a set of sensible parameters must be

found. Table 4.2 gives a list of sensible parameters with which the washing parameters from table 4.1 can be found.

Table 4.2: List of sensible parameters which give an impression of the washing process

	Sensor output	Washing parameters
Physical	Temperature	Temperature
	Flow	Turbidity
	Conductivity	Water quality, rinsing effectiveness, turbidity
	Dynamic surface tension	Detergent concentration
	Torque on tub-motor	Amount of laundry, water level
Concentrations	pH	pH
	H_2O_2	Bleach activity
	Ca^{2+}, Mg^{2+}	Hardness, builder functioning
	Enzymes	Enzymatic cleaning effectiveness, specific soil detection

The parameters listed in this table are the starting point for the summary in this chapter. Torque sensor principles are omitted because such sensors will probably not be placed in the sensor array, but will be realized in combination with the tub motor. Sensors for measuring the type of laundry (colour, fabric) are omitted as well because no good sensors for the determination were reported in literature. Some techniques for fabric type determination are based on the water resorption characteristics (from a water level versus applied water curve), so they will probably not be placed in the sensor array.

4.2. Temperature

Most of the sensor principles are temperature dependent, and need to be corrected for the local temperature. The number of temperature dependent phenomena is the reason for the large amount of temperature sensing principles based on these phenomena.

Besides this direct interest of temperature sensing, there are some other sensing principles which make use of temperature determinations. Examples can be found in flow measurements and specific heat capacity. The specific heat capacity at constant volume of a substance is defined as [32]:

$$C_{V.spec} = \left(\frac{\delta U}{\delta T}\right)_V \frac{1}{M} \qquad (4.1)$$

where U is the internal energy, T the temperature and M the mass of the substance. Because a change in internal energy can be identified with the heat supplied at constant volume ($q_{supplied} = \Delta U$), the previous equation can be used to determine the specific heat capacitance. A measured quantity of heat is supplied to the sample

(electrically for example) and the resulting increase in temperature is observed. The ratio of supplied heat and temperature increase results in the heat capacity.
It can be considered if this method is useful to determine information on the washing load. The amount of laundry and laundry type will change the heat capacity of the total tub load (water plus laundry).

a) Glass thermometer, thermal expansion
The glass thermometer is based on the relation:

$$\frac{P \cdot V}{T} = \text{Constant} \tag{4.2}$$

where P the pressure, V the volume and T the temperature. At constant pressure, the volume of a certain amount of liquid (usually mercury) changes linearly with the temperature.
To make the volume change visible for the human eye, the liquid is stored in a small capillary, so

$$\Delta T = \frac{P \cdot A}{\text{Const}} \cdot \Delta h \tag{4.3}$$

with A the cross section of the capillary and Dh the change in the mercury column length.

b) Thermistor, thermoresistive effect
Thermoresistive elements are sometimes called bolometers. There are semiconductor and metal based bolometers. The bulk conductivity of many semiconductors is dependent on de temperature of the device. This has led to the development of thermistors which can be used to measure local heat production (calorimetry).
There are in fact three categories of thermistors: the ceramic negative temperature coefficient (NTC) type, fabricated by high-temperature sintering of certain metallic oxide mixtures, the positive temperature coefficient (PTC) type, made by sintering barium and strontium titanate mixtures, and the single crystal doped semiconductor (silicon) type, which has also a positive temperature coefficient [7].

The temperature coefficient of a thermistor is:

$$\alpha = \frac{1}{R_T}\left(\frac{dR_T}{dT}\right) = -\frac{\beta}{T^2} \tag{4.4}$$

which is a temperature-dependent coefficient that decreases with increasing temperature. A typical value for this coefficient at 300 K is

$$\alpha = -0.044^{\circ}\text{C}^{-1}.$$

When accuracy is required and an offset is undesired, the thermistor is placed in a bridge circuitry.

c) Pt100, thermoresistive effect

While the thermistor resistivity has an exponential dependency on temperature, metal strips do have an almost linear variation in a certain temperature range.
With equation (3.1) the linear relation between temperature and resistivity of a platinum strip of 100W (at 0°C) was already given. Applications of Pt100 elements are in a bridge set-up.

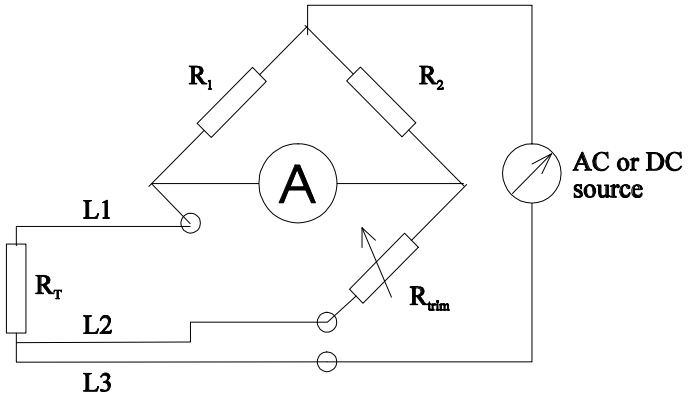


Fig. 4.1: A three-wire Pt100 element in a bridge circuitry

To remove the effect of lead resistances, the element is supplied with three wires. Two of them are connected to the same side of the Pt resistor. Figure 4.1 shows a three wire Pt100 in a bridge. Leads L1 and L2 are in opposite branches of the bridge, when the bridge is trimmed (no current through ampere meter) the resistances are:

$$\frac{R_1}{R_T + R_{L1}} = \frac{R_2}{R_{trim} + R_{L2}}. \qquad (4.5)$$

So when $R_1 = R_2$ and $R_{L1} = R_{L2}$ then $R_T = R_{trim}$ and all three wire resistance are eliminated.
Problems with Pt100 elements come from the self heating when a current flows trough the device. This can be avoided by measuring in a pulsed way.

d) Spreading resistance, thermoresistive effect

Because of the accuracy and reliability, the spreading resistance technology temperature devices are an attractive alternative to the more conventional sensors using NTC or PTC thermistors.
Commercially available discrete semiconductor temperature sensors [29], are made with the spreading resistance technology. They have a positive temperature coefficient and a virtually linear temperature characteristic.
These sensors use n-type silicon with a doping level between 10^{14} and $10^{15}/cm^3$, providing a normal resistance at 25°C of 1kW. The construction of the basic sensor chip is shown in figure 4.2. The chip size is about ½ × ½ × ¼ mm. The upper plane of

the chip is covered by an insulating silicon dioxide layer in which a hole of about 20 µm has been etched for a metal contact to the silicon. The bottom plane is entirely metallized.

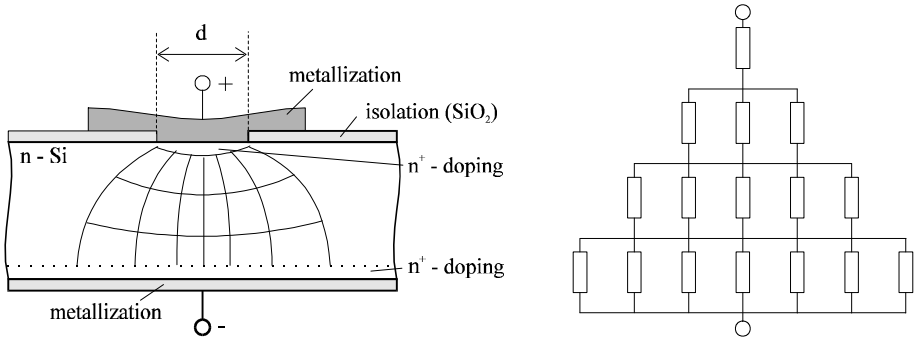


Fig. 4.2: Spreading resistance measurement device and equivalent circuit [29]

This structure results in a conical current distribution through the crystal, hence the name "spreading resistance". The temperature dependency becomes:

$$R_T = R_{ref}\left[1 + A(T - T_{ref}) + B(T - T_{ref})^2\right] \qquad (4.6)$$

with R_T the resistance at temperature T and R_{ref} the nominal resistance at the reference temperature T_{ref}. The coefficients A and B are geometry and doping dependent, typical values are $A = 7.9 \cdot 10^{-3}\ K^{-1}$ and $B = 1.9 \cdot 10^{-5}\ K^{-2}$ at $T_{ref} = 25°C$.

e) Thermocouple, thermoelectric effect

If two different metals are connected in a closed circuit with their two junctions at different temperatures, a current will be observed [7]. The Seebeck thermal emf, responsible for this current flow, depends on the types of metal involved and is approximately proportional to the temperature difference between the two junctions.
In the simplest form a thermocouple consists of two dissimilar metals A and B shown in figure 4.3 with an open circuit in wire B to measure the emf.

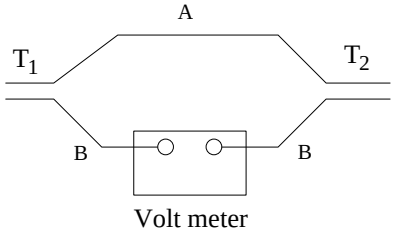


Fig. 4.3: Measurement of a Seebeck thermoelectric emf

The Seebeck emf is related to the absolute junction temperatures T_1 and T_2 by

$$V = \alpha(T_1 - T_2) + \gamma(T_1^2 - T_2^2) \qquad (4.7)$$

where α and γ are constants for the thermocouple pair. Since in practice the quadratic dependence is not too strong, the emf can closely be approximated by a linear relation if the temperature difference (T_1-T_2) is not too large.

f) Thermochemical effect

Thermochemical indicators make use of the temperature sensitive chemical changes in some substances.

The rapid colour changes that some liquid crystals show occur with relatively small temperature changes. This enables one to measure surface temperatures either by painting or spraying a liquid crystal substance on a surface. In some applications plastic-film encapsulated liquid crystals are used, for example for glass temperature indication (wine bottle) or use in combination with a thermoresistive actuator as battery quality indicator.

Registration of the effect is always optical.

g) Pyroelectric effect

In certain types of materials with noncentrosymmetric structure, polarization changes strongly with temperature. Many piezoelectrics, like ZnO, are also pyroelectric [31]. Other examples are lead zirconate-titanate materials.

Under steady state conditions, the surface charge created by the polarization is neutralized by external charges (due to leakage currents) and no emf is observed across the material. However, if the temperature is changed, the state of polarization changes and an external emf will be observed. This is the pyroelectric effect [7].

h) pn-junction

An understanding of the temperature characteristics of p-n junction diodes can be gained by considering the current I at constant voltage V of a silicon diode in a forward biased operation [4]:

$$I = \frac{KT^r}{\eta} \cdot e^{\frac{qV - \phi_g}{kT}} \qquad (4.8)$$

in which

- K is a constant for the junction
- r is a constant depending on the semiconductor and impurity concentration and is related to the temperature dependence of the mobility of the minority carriers
- η the ionisation factor
- ϕ_g the bandgap energy at 0 K.

The diode voltage at constant current follows from this equation and is:

$$V = \frac{\phi_g}{q} + \frac{kT}{q}\left[\ln(I) - \ln\left(\frac{KT^r}{\eta}\right)\right] \qquad (4.9)$$

The characteristics of a diode depends on the structure of the junction which can vary considerably from type to type. So an accurate calibration of the temperature dependency is required. Besides that there is no linear relation with temperature.

i) PTAT

Better results than using a single diode can be obtained with transistors or transistor pairs. For a bipolar junction transistor, the temperature dependency of the V-I characteristics resembles that of the diode, it follows from the transistor operation:

$$I_c = I_s \cdot e^{\frac{qV_{be}}{kT}} \tag{4.10}$$

with

$$I_s = \frac{KT^r}{\eta} \cdot e^{-\frac{\phi_g}{kT}} \tag{4.11}$$

(all constants comparable to the diode operation) which results in:

$$V_{be} = \frac{\phi_g}{q} + \frac{kT}{q}\left[\ln(I_c) - \ln\left(\frac{KT^r}{\eta}\right)\right]. \tag{4.12}$$

With a pair of identical transistors (same constants f_g, K, T, q, h and r) the base-emitter voltage difference depends linearly on temperature:

$$\Delta V_{be} = V_{be1} - V_{be2} = \frac{kT}{q}\ln\left(\frac{I_{c1}}{I_{c2}}\right) \tag{4.13}$$

If the collector currents are dissimilar, the output voltage is proportional to the absolute temperature (PTAT sensor). This condition is served by an a-symmetric current mirror. Figure 4.4 shows the principle.

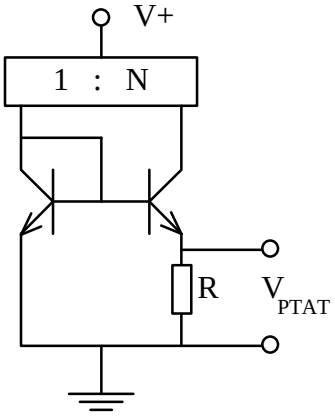


Fig. 4.4: A practical PTAT temperature sensor set-up

A relation for the temperature dependency can be calculated by substituting (4.10) and (4.11) in (4.13), the output voltage becomes:

$$V_{PTAT} = V_{be1} - V_{be2} = \frac{kT}{q} \ln\left(\frac{I_{s1}}{I_{s2}} \cdot N\right) \qquad (4.14)$$

with N the ratio of collector currents. This voltage is proportional to the temperature over a wide range.
Besides bipolar PTAT circuits, MOSFET based PTATs are possible as well.

4.3. Flow

To get an impression of the stirring in a washing machine (maybe of interest for sensor behaviour) the flow can be measured. In this subsection an (incomplete) list of flow measurement techniques is given. Some of them are impossible to perform in a washing process, others are more easy.

a) Time of flight
When a liquid (or gas) is locally heated by a heat pulse, the time to detect this pulse at a distance x is a value for the flow. Other markers like small bubbles are reported as well.

b) Anemometric measurement
With anemometry, the cooling down of a heated element is used to calculate the flow of a heat conducting medium.

c) Pressure gradient
The pressure gradient technique for measuring the instantaneous flow velocity is based on a mathematical relationship between the velocity and the pressure gradient along a vessel. It can be shown that for a cylindrical rigid tube the instantaneous fluid

velocity v averaged across the tube is related to the instantaneous pressure gradient along the tube by:

$$\frac{-\Delta P}{\Delta x} = \frac{1.1\zeta}{g}\frac{dv}{dt} + \frac{12.8\mu v}{ga^2} \qquad (4.15)$$

where DP/Dx is the pressure gradient, z is the fluid density, g the acceleration constant, μ the viscosity, a the inner diameter and v the average flow velocity [7]. This method can only be used in tubes. To increase a pressure gradient, an obstruction is sometimes introduced in the tube.

d) Mechanical

Mechanical methods to determine flow use a rotameter which drives an electromagnetic emf transducer (dynamo). The output current of this transducer is proportional to the rotation velocity of the rotor and so to the flow. At zero flow the output current is zero as well (because it is a self generating transducer). The disadvantage is that this sensor has mechanical parts.

e) Electromagnetic

When a conductor is moved through a magnetic field, as illustrated in figure 4.5, an emf is generated with a value proportional to the velocity. When the conductor is a fluid moving with uniform velocity v, then the emf generated across the diameter EE' for a uniform magnetic flux density B is given by

$$V = 2 \cdot 10^{-4} \cdot a \cdot B \cdot v \qquad (4.16)$$

where B is in gauss, v in m/sec and a in meters.

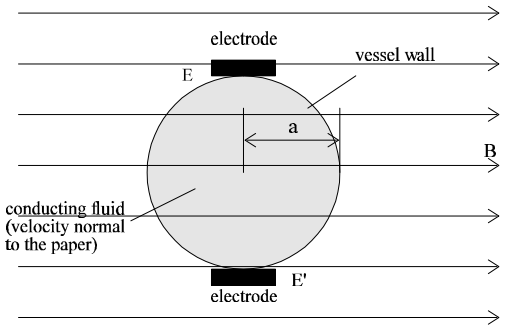


Fig. 4.5: Principle of electromagnetic flow meter

f) Ultrasonic

In the set-up as drawn in figure 4.6, a liquid flows through a tube with a velocity v. An ultrasonic sound source is applied to the tube with frequency f_s and angle Q. The reflected sound has a frequency f_r and angle j.

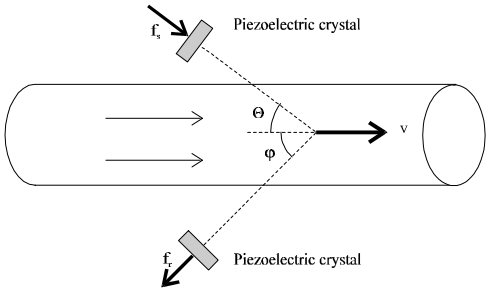


Fig. 4.6: Set-up of a Doppler shift measurement

Assuming that the used sound velocity is much smaller than the velocity of light, the Doppler shift in the frequency is, as calculated in reference [7]:

$$\Delta f = f_s - f_r \approx \pm f_s(\cos\Theta + \cos\varphi)\frac{V}{c} \qquad (4.17)$$

with the minus and plus signs have been introduced to account for the direction of the flow. This method is at present very popular in the medical practice for the measurement of blood flow in human vessels.

g) Indicator dilution methods
The operation of this wide scale of methods is based on the measurement of the dilution of an injected indicator. For proper operation an accurate model of the diffusion and flow behaviour of the indicator is necessary. Examples with different indicators are dye dilution, thermal dilution and conductivity dilution methods (as in use for the measurement of cardiac output).

4.4. Conductivity

By measuring conductivity, an impression is obtained of the state of rinsing cycles or about the soil level in the washing tub. Besides that some conductivity sensors can be used as concentration sensors when they are used in combination with a selective membrane.

a) Two-points set-up
A standard conductivity measurement is based on the measurement of the potential/current relation (impedance) of an electric current through an electrolyte. In a two points set-up the electrodes that generate the current are used for measuring the potential as well.

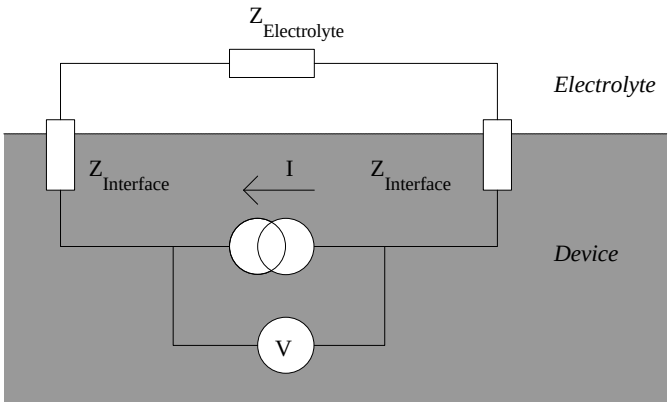


Fig. 4.7: Conductivity measurement in two point set-up

The problem with this method is that the two relative instable interface overpotentials are in series with the potential difference induced in the electrolyte which gives an unknown error in the measured impedance.
The insulator Ta_2O_5 has a very low oxide/solution impedance, so a two points conductivity measurement based on a Ta_2O_5 probe is an attractive alternative [13]. Sometimes the probe is realized as an interdigitated finger electrode.

b) Four points set-up
The problem with a two point conductivity set-up is that the overpotentials of the working electrodes are disturbing the measured potential, and so the measured conductivity. In a four points set-up, the current loop and the potential sensing are realized in a separate circuit.

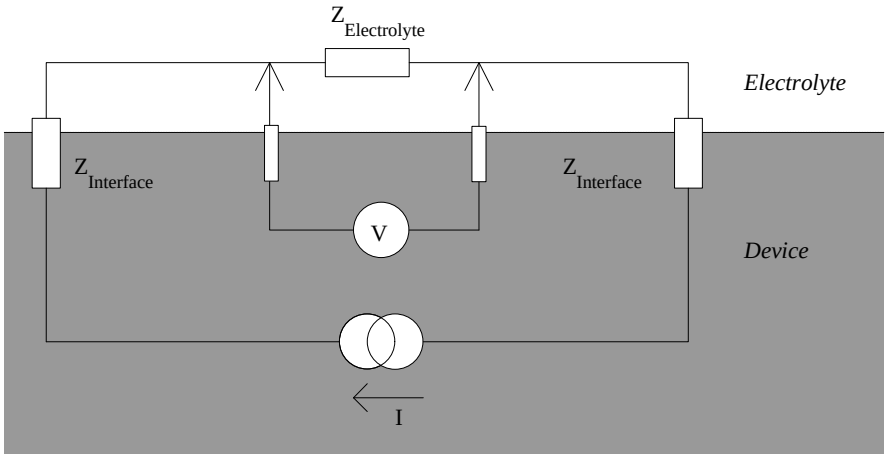


Fig. 4.8: Conductivity measurement in four points set-up

The impedances of the measurement loop do not affect the measurement when this loop is sufficiently high-ohmic. Instable electrode potentials will not affect the measurement if the frequency of the AC current source is chosen high enough.
The potential sensing is realized using either capacitive probes (Ta_2O_5 cell or ISFETs) or metal strips [25].

c) Using an ISFET
In the small signal model of the ISFET, the conductivity of the electrolyte is one of the parameters. This can be used to obtain the conductivity from the -3 dB frequency [24]. To remove the effect of the relatively low bulk resistance (which results in a very high cut-off frequency), a small window for the ISFET is used. This final cut-off frequency is in the range of 100 to 500 kHz.

4.5. Dynamic surface tension

The dynamic surface tension (DST) of a liquid is related to the surfactant concentration. This phenomenon is being used by Alex Volanschi who is currently developing a dynamic surface tension sensor [10]. The operation of these sensors is based on the frequency dependency of electrolytically generated gas bubbles on the surface tension.
The DST electrodes are not simple metal films. Two configurations are being evaluated. The first one is the cavity electrode. Bubble nucleation is controlled here by the geometric structure of the electrode. This specific structure is a piramid shaped hole which is made by an anisotropic etch of silicon (KOH etch) before metal evaporation. The second one is the "gas phase nucleation core" electrode where the nucleation is controlled by an instantaneous amount of gas. This device requires an isotropic etch of silicon to make the gas core in the substrate.

4.6. Hydrogen peroxide concentration

Some hydrogen peroxide determination methods are well developed in glucose sensors where a GOD-membrane catalysis the glucose concentration to an equivalent hydrogen-peroxide concentration. In these systems, the GOD membrane guarantees the selectivity. The hydrogen peroxide concentration can be measured by:

a) Amperometric method
A platinum electrode based on the electrochemical monitoring of hydrogen peroxide concentration is most widely used for biosensors at present. The Pt electrode is biased at 0.7 V versus an Ag/AgCl electrode. This method, however, suffers from interferences of electro-oxidizable compounds in the solution (such as Fe^{2+}), so a high performance sensor is not possible [14].

b) Chrono amperometric detection
After applying a potential step across an electrolyte-electrode interface, the Cottrell equation (3.3) can be used to determine the concentration of H_2O_2 from the measured current. This step must be high enough to deplete the H_2O_2 concentration completely at the surface according to

$$H_2O_2 \leftrightarrow O_2(g) + 2H^+ + 2e^- \qquad 0.682\ V. \qquad (4.18)$$

Because a slope is detected instead of an absolute current, the reference electrode might be omitted and a two-strip set-up can be used [6]. This is only true when the applied half-cell potential is known to guarantee reaction (4.18).

c) Potentiometric method

Good results are reported [30] using a carbon electrode loaded with Perovskite-type oxides like $LaCo_xNi_yMn_zO_3$. A logarithmic variation with hydrogen peroxide concentration is observed. Dependent on the used oxide contaminants, the reaction:

$$H_2O_2 + 2H^+ + 2e^- \leftrightarrow 2H_2O(l) \qquad (4.19)$$

can be selected. The carbon with a perovskite-type oxide is placed on a conducting material. A current is applied and the EMF is being measured in a half cell set-up (potentiostat).

From the given reaction equation it can be concluded that the pH must be constant during measuring.

d) Volumetric titration

The following reaction [33] occurs when potassium permanganate solution is added to hydrogen peroxide solution acidified with dilute sulphuric acid:

$$2MnO_4^- + 5H_2O_2 + 6H^+ \leftrightarrow 2Mn^{2+} + 5O_2 + 8H_2O(l) \qquad (4.20)$$

where MnO_4^- has an intense purple colour and Mn^{2+} hasn't. This is a classical example of a volumetric redox titration. In a laboratory set-up the end point is easy to be detected optically when the purple droplets coming from the burette do not disappear anymore.

e) Chemiluminescence

Certain compounds (molecules) can be detected by mixing them with a reagent with which the molecules react to form exited molecules which decay spontaneously with photo emission [34]. For hydrogen peroxide some of those reagents are available. This method requires a large optical system.

f) UV absorption

Ultraviolet absorption is a technique which uses the emitted light of exited molecules as well. But now the molecules are exited by supplying energy in the form of ultra violet light.

4.7. Measuring the pH and acid concentrations

The words terminology "acid concentration" and "pH" are both considering acids but are quite different. The pH is the logarithm of the activity of free protons in a solution while the acid concentration concerns the applied amount of a certain (weak) acid. The first determination method described in this subsection gives information about the pH, the other one concerns the acid concentration.

Measurement of pH:

a) Potentiometric detection
Interface potentials can be used to obtain an electrical signal from ion activities. The major part of pH sensors detect proton concentrations by making use of a potentiometric technique.

The pH glass electrode
An application of a pH sensor using an electrochemical cell is the pH glass electrode. This is an ISE (Ion Selective Electrode) with a H^+ selective glass. Inside the electrode there is a buffered KCl solution with an Ag-AgCl or calomel electrode as a reference. At the inner side of the glass there is a constant potential because of the constant ion activities in the inner solution. At the outer side of the glass a pH dependent diffusion potential occurs which can be measured with respect to an external reference electrode. The diffusion potential is theoretically:

$$E = E^0 + \frac{RT}{F} \ln a_{H^+} \qquad (4.21)$$

and is called the Nernst potential. Because the pH is defined as:

$$pH = -\log a_{H^+} \qquad (4.22)$$

the result is a dependency of 59 mV per decade.

The ISFET
The ISFET has the advantage that it is not made of fragile glass and that it is smaller than the glass electrode. Because the operation is based on surface potentials, rather than diffusion potentials, the operation is faster than in the case of the glass electrode. The disadvantage of needing a reference electrode is just as with the glass electrode still a problem. It would be nice to have a solid state reference (a REFET) which can be used in a differential pH measurement using a pseudo reference.

Measurement of acid concentrations:

b) Indication by performing an acid-base titration

A bare ISFET measures the activity of protons. With a strong acid this is a direct indication for the acid concentration. When having a weak acid the amount of free protons is only a fraction of the total acid concentration, because of the acid equilibrium

$$HA \leftrightarrow H^+ + A^-. \tag{4.23}$$

The state of the equilibrium is given by the association constant:

$$K_a = \frac{[H^+][A^-]}{[HA]}. \tag{4.24}$$

By applying OH^--ions to the chemical system, which can be done by either a volumetric or a coulometric titration, the pH varies with a characteristic shape: the titration curve. From the end point in this curve, which is the moment where the pH has a very abrupt change, the acid concentration can be determined.

An application is the coulometric sensor-actuator device [5] where hydroxide ions are electrochemically generated and the pH is monitored by an ISFET. Using a constant cathodic current i_c, the time to reach equilibrium is:

$$t_{end} = \frac{\pi D_{HA} F^2 A^2 C_{HA,bulk}^2}{4 i_c^2} + \frac{(\pi - 2) x_s^2}{2\pi D_{OH}} + \frac{F C_{HA,bulk} x_s A}{i_c} \tag{4.25}$$

with the first term the Sand equation (3.6), x_s the distance between the actuator and sensor, D_{OH} the diffusion constant of hydroxide ions and $C_{HA,bulk}$ the concentration of HA in the bulk.

4.8. Calcium concentration and hardness

Historically "hardness" was defined in terms of the capacity of water to precipitate soap [35], which has an undesirable effect on washing effectiveness. Soap is precipitated by most ions with multiple charges. Because calcium and magnesium generally exceed the concentration of other cations, the hardness is defined as the total calcium and magnesium concentration in terms of the calcium carbonate equivalent.

Most of the methods listed here are selective for calcium with respect to magnesium but they are widely used for hardness determinations.

a) Volumetric titration with EDTA
A particularly property of EDTA (EthyleneDiamineTetraAcetate) as a titrant is that it combines with metal ions in a 1:1 ratio regardless of the charge of the cation. The general equilibrium is:

$$M^{n+} + HY^{3-} \leftrightarrow MY^{(n-4)+} + H^{+} \qquad (4.26)$$

with Y^{4-} the EDTA-ion and M the metal ion. According to these complexes with a large number of metal ions, this method is not selective for calcium and magnesium.
Because of its pH dependence, EDTA titrations are generally performed in buffered solutions (for water hardness a buffered pH of 10). The indicator can either be calmagite or eriochrome black T. Often a small concentration of the EDTA complex of magnesium is included in the buffer to assure the presence of sufficient magnesium ions to improve indicator action.
Some test kits for determining the hardness of tap water work in this way.

b) Volumetric titration with Patton and Reeder's indicator
Patton and Reeder's indicator (HHSNNA) permits the determination of calcium in the presence of magnesium, and finds application in the determination of the hardness of water [33].

c) Coulometric titration
This method makes use of the amine mercury(II) complex of EDTA-acid (H_4Y). The complexing agent EDTA is released to the solution as a result of the following reaction of the mercury electrode:

$$HgNH_3Y^{2-} + NH_4^{+} + 2e^{-} \leftrightarrow Hg + 2NH_3 + HY^{3-} \qquad (4.27)$$

which is followed by reaction (4.26).
Because the mercury chelate is more stable than the corresponding complex with calcium (also zinc, lead or copper), complexation with this ion will not occur until the electrode process frees the ligand.

d) Potentiometric detection
Analogous to the measurement of protons, the detection of calcium ions can be done using interface potentials.

Liquid membrane electrode
Figure 4.9 shows the construction of a commercial liquid membrane electrode that is selective for calcium ions [35].

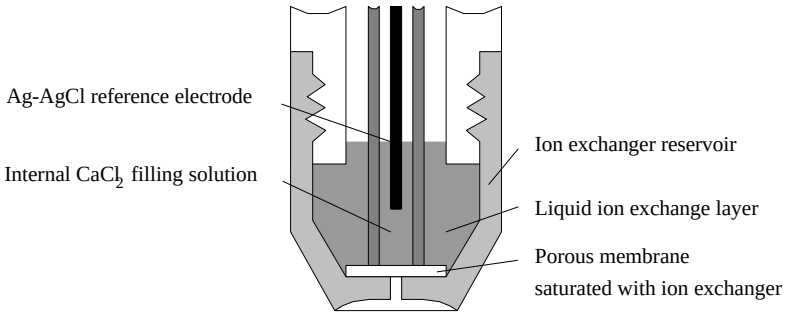


Fig. 4.9: Liquid membrane calcium electrode

The ion exchanger is an aliphatic diester of phosphoric acid dissolved in a polar solvent. The diester contains a single acidic proton, thus two molecules are required to bond a divalent calcium cation.

ChemFET
Commercially available ionophores can be used to make a calcium ion selective PVC membrane. This membrane, in combination with an ISFET, gives a calcium ChemFET. Although Nernstian responses can be observed, ChemFETs in general do not give promising results for the use in the washing sensor array.

4.9. Enzyme detection

Detection of enzymes (or peptides in general) generally requires a two phase method: first the peptide is specifically bonded to a membrane and secondly this reaction is being detected by an electronic device. In case of a reaction which releases protons, an ISFET can be used for detection (the ENFET). When the ionic strength in the membrane is drastically influenced by the peptide reaction, a conductivity sensor is more adequate.
An exhaustive list of detection principles of enzymes (or peptides in general) is omitted here.

4.10. Summary

The methods evaluated in this chapter are summarized in the tables 4.3 and 4.4 for physical and chemical parameters respectively.

Table 4.3: Summary of methods for determination of physical parameters

Temperature	Flow	Conductivity	Dyn. surface tension
Thermal expansion	Time of flight	Two-points set-up	Bubble electrode
- glass thermometer	Anemometry	Four points set-up	
Thermoresistive effect	Pressure gradient	Using an ISFET	
- thermistor	Mechanical		
- Pt100	Electromagnetic		
- spreading resistance	Ultrasonic		
Thermoelectric effect	Indicator dilution		
- thermocouple			
Thermochemical effect			
Pyroelectric effect			
pn-junction			
- single pn-junction			
- PTAT			

Table 4.4: Summary of methods for determination of physical parameters

H_2O_2	pH and acid conc.	Ca^{2+} and hardness	Enzyme detection
Amperometric method	Potentiometric detection	Volumetric titration	
Chrono amperometry	Acid-base titration	- EDTA	
Potentiometric method		- Patton and Reeder's ind.	
Volumetric titration		Coulometric titration	
Chemiluminescence		Potentiometric detection	
UV absorption			

5. Sensor classification as electronic devices

The vision of modulating devices given in chapter 2 can be used to make a list based on the device that is modulated [27]. Self generating devices can be implemented as current and voltage sources. Here the most common electronic devices are chosen like resistors and capacitors and a list is given of the sensor applications developed up to now.

5.1. Passive elements

5.1.1. Resistors

Resistor based sensors are easy to use because they give an immediate (current) response on an applied voltage. Capacitors and inductances need a more complex set-up to determine their value, they are generally placed in a resonance circuit or an RC- or RLC-circuit. However, a certain time is needed to determine the resonance frequency, the response time or the cut-off frequency.

a) Temperature
The thermoresistive effect of metal strips was already mentioned. The Pt-100 is an example of this category. Other materials like metal oxides can be used for thermoresistive set-ups as well.

b) Chemo-resistors
Standard metal oxide gas sensors consist of a sintered block of the oxide which is heated to a few hundred degrees centigrade. Surrounding gases react with the oxygen on the hot surface causing changes in the resistivity of the material. Gas sensors based on this principle and employing oxides of tin, zinc, zirconium or titanium and with proper doping are known to be sensitive to many types of gases. Metal-oxide gas sensors can be fabricated using thin (silicon) and thick film technology [4].

5.1.2. Impedances

A sensor like the interdigitated finger structure can not be placed in the subsection with resistors, because it is an impedance. The devices mentioned in subsection 3.1.4.c) concerning conducting polymers can be used as an impedance based sensor. When placed on a finger structure, the conductance of the polymer can be measured in the impedance of this finger structure. The conductivity can be influenced by gasses and ions [4].

5.1.3. Capacitors

The dielectric constant of a material is not really a constant, but a function of some physical parameters like temperature and adsorbed water. When placed between two metal plates or on a finger structure it can be used for capacitive detecting purposes.

a) Temperature
The dielectric constant of some materials is dependent on temperature. So the capacitance of a parallel plate capacitor can be used for monitoring temperature.

b) Humidity
The capacitance of a planar capacitor depends on the amount of the moisture adsorbed on the dielectric material. This effect can be used in a humidity sensor.

5.1.4. Inductances

Inductances are hard to realize in micro technology, maybe that is why no significant chemical and physical sensitive coils were reported in literature. In theory it must be possible to determine all kind of variations in the magnetic permittivity of materials due to all physical and chemical influences. Temperature, moisture and deposition measurements must be possible, but the size of the fluctuations in the μ_r is very small.

5.1.5. Diodes

The applications of diodes in sensors can be separated into two types. One widely applied physical sensitive diode is the temperature sensor. A chemical sensitive diode-based device is the ion controlled diode.

a) Temperature
The diode equation (4.8) contains the absolute temperature, so the behaviour of the diode is dependent on temperature (see section 4.2.h) for details).

b) ICD
The ion controlled diode (ICD) was mentioned in section 3.2.5.a) as an electrolyte/-insulator/semiconductor structure. The ICD uses the phenomenon that the space charge is modulated by the ion-concentration of an electrolyte.
The advantage is that the wires for electronic connection are at the back-side of the device and will not be in contact with the electrolyte (figure 3.10).
ICD's are reported with valinomycin for potassium sensitivity and silicon nitride for pH sensitivity [23]

5.2. Active elements

5.2.1. Bipolar transistors

a) Temperature
In section 3.2.5.i) the use of a bipolar junction transistor in a proportional-to-absolute-temperature (PTAT) set-up was evaluated.

b) Chemical dependency
The ICD described above looks like a bipolar transistor, but is not used in a transistor mode (common emitter mode or something).
Section 3.2.3.b) referred to the transistor technique where one of the three areas in the transistor is exchanged by an electrolyte [11].

5.2.2. MOS transistors

When a MOSFET is unsaturated, this means that $V_D < V_G - V_T$, the behaviour can be described by [36]:

$$I_D = \mu \frac{W}{L} C_{ox} \left((V_{GS} - V_T) V_{DS} - \frac{V_{DS}^2}{2} \right) \tag{5.1}$$

$$V_T = V_{FB} - \frac{Q_B}{C_{ox}} + 2\phi_f \tag{5.2}$$

$$V_{FB} = \frac{\Phi_M}{q} - \frac{\Phi_{Si}}{q} - \frac{Q_{it} + Q_f}{C_{ox}} \tag{5.3}$$

with

- I_D the drain current;
- μ the electron mobility in the channel;
- W/L the channel width to length ratio;
- C_{ox} the oxide capacitance;
- V_T the threshold voltage;
- V_{FB} the flatband voltage;
- Q_B, Q_{it}, Q_f the bulk depletion charge, the interface traps and the fixed oxide charge per unit area;
- ϕ_f the Fermi potential difference;
- Φ_M, Φ_{Si}, the metal and silicon work functions
- q the unity of charge.

The dependency on the physical parameter Φ_M is essential for the applications of most of the MOSFET structures in chemical sensors. Variations in this parameter can directly (1:1 relation) be measured in the threshold voltage.

a) Gas sensors, ADFET, OGFET and SAFET

It was found that the metal work function changes with the contamination of the metal. An application is the use of a palladium gate, were the amount of adsorbed hydrogen gas influences the metal work function. So the threshold voltage V_T is a function of the hydrogen gas concentration.

When the gate metal is omitted and the device exposed to a gas, an Open Gate Field Effect Transistor is made (OGFET). This device gives responses to polar gasses like water vapour and methanol.

An improvement is obtained when the oxide layer is very thin (5 nm). For thicknesses below this value the device responds to all kind of gasses which have a permanent net dipole moment, such as H_2, NH_3, HCl, CO, NO, NO_2 and SO_2. This device is called the ADFET [36].

The problem with these devices is that the gate is badly defined. A solution is the use of the SAFET, which has an oxide layer which is partially covered by a metal gate. At the uncovered side, a dependency on polar gasses (water, acetone, alcohols) is observed.

b) Humidity sensor, CFT

The Charge Flow Transistor (CFT) is a MOS-based field effect transistor with the metal gate placed as a ring around a resistive layer. This layer is humidity dependent, so an applied gate voltage appears integrated at the oxide surface, and will as such be measured by the field effect transistor.

c) Pressure sensor, PRESSFET

This device contains a floating (mechanical movable) plate hanging above the oxide of an ISFET structure. The influenced parameter is the air gap capacitance which becomes a virtual oxide capacitance in equation (5.1).

d) pH Sensor, ISFET

The set-up for an ISFET looks like that of the described gas-sensitive FETs but now the oxide is in contact with a liquid. The gate is a reference electrode in the electrolyte. For the flatband voltage, equation (5.3) is still valid but looks slightly different:

$$V_{FB} = E_{ref} - \psi_0 + \chi^{sol} - \frac{\Phi_{Si}}{q} - \frac{Q_{it} + Q_f}{C_{ox}} \qquad (5.4)$$

where E_{ref}, the reference electrode potential relative to vacuum, now contains the metal work function, while the additional term $-\psi_0+\chi^{sol}$ describes the interface potential at the electrolyte silicon interface. The factor χ^{sol} is the surface dipole moment of the solution and ψ_0 is the actual pH dependent parameter according to:

$$\frac{\delta\psi_0}{\delta pH} = 2.303\frac{kT}{q}\alpha \qquad (5.5)$$

with the factor α as a selectivity factor (theoretically between 0 and 1) being:

$$\alpha = \frac{C_\phi}{C_{diff} + C_\phi} \qquad (5.6)$$

where C_f is the adsorption pseudocapacitance [37].
The pH dependency is the result of the charged sites of OH^- and H^+ at the oxide surface. It appears that Ta_2O_5 has more sites than SiO_2 (a higher a-value) so the first one has now become standard for ISFETs at the biosensors group of the University of Twente.

e) Reference probe, REFET
For more elegant use of an ISFET, a modified ISFET is necessary to form a differential set-up which gives a pure pH output. This device, a REFET, should be sensitive to all parameters, except for the pH, without losing the electronic contact to the electrolyte. Only some devices are reported with lowered pH sensitivity but a good REFET is still not available.

f) Ion sensor, ChemFET
This device was already mentioned in previous chapters. In this context it must be seen as an ISFET with an ion selective threshold voltage.

g) Enzyme based FETs, ENFET, IMFET, BIOFET
When a ChemFET is taken with a immobilized enzyme membrane, the chemical reactions that are specifically catalysed can be monitored as a pH variation. This is the ENFET.
Other devices (IMFET) have specific immobilized receptors which give a antigen-antibody response. This immuno-reaction can be monitored by the ISFET. Besides that the response can be generated in a bio-active reactor (for instance containing bacteria): The BIOFET.

h) Conductivity sensor
In the small signal model of the ISFET, the electrolyte conductivity between ISFET and reference electrode becomes important [24]. The cut-off frequency is:

$$f_{-3dB} = \frac{1}{2\pi R(C_{GD} + C_{GS})} \qquad (5.7)$$

with R the resistivity of the electrolyte and C_{GD} and C_{GS} the gate to drain and gate to source capacitances respectively. A common range for this frequency is 0.1 MHz to 5 MHz which can be chosen by changing the geometry of the structure.

5.2.3. Crystal

Quartz crystals have the possibility to vibrate when they are activated by a feed forward electronic circuit. Placed in an oscillator the rather high frequency (about 10 MHz) is very stable, and is often used as clock frequency in many electronic applications.

a) Crystal oscillator sensors

The resonance frequency of crystals is not only dependent on the properties of the material, but also on the mass of the connecting electrodes. This is why vibrating crystals are sometimes used to determine the mass of deposited material. An example is the monitor-crystal in a vacuum clock for (for example) metal deposition detection purposes.

Crystal gas sensors are also reported. They consist of a crystal, coated with materials used in gas-chromatography. This coating will adsorb gasses and the mass will thus be increased. The result is an increase in the oscillation frequency. The same is possible in liquids.

b) SAW devices

Another field of crystal applications are the SAW (surface acoustic wave) devices which are the combination of a crystal actuator and sensor. SAW devices give information about the propagation of acoustic waves across a surface.

5.3. Summary

Table 5.1: Overview of electronic devices with their chemical and physical sensitivities

Device	I-V relation	Sensitive parameter	Dependent on	Name
Resistor	$V_R = I_R \cdot R$	R	Temperature Ions Gasses	Pt-100 Chemi-res. Chemi-res.
Impedance	$\overline{V} = \overline{I} \cdot \overline{Z}$	Z	Conductivity	Finger elect.
Capacitor	$I_C = C \cdot \frac{dV_C}{dt}$	ε_r	Temperature Moisture	
Inductance	$V_L = L \cdot \frac{dI_L}{dt}$	μ_0	?	
Diode	$I_D = I_0\left(e^{\frac{qV_d}{kT}} - 1\right)$	kT/q I_0	Temperature Ions	 ICD
BJT	$I_C = I_S e^{\frac{qV_{BE}}{kT}}$	kT/q	Temperature	PTAT
MOSFET	$I_D = \mu \frac{W}{L} C_{ox}\left((V_{GS} - V_T)V_{DS} - \frac{V_{DS}^2}{2}\right)$	$V_T(\Phi_M)$	Polar gasses	OSFET, SAFET, ADFET
		$V_T(\psi_0)$	pH	ISFET
		$V_T(\psi_0)$	Ions	ChemFET
		$V_{GS\text{-}eff}$	Humidity	CFT
		C_{ox}	Pressure	PRESSFET
Crystal		f_{res}	Mass	Deposition sensor

6. Conclusions

The overview given in this report was focused on sensors for washing sensor array applications. This is why gas sensors and optical techniques are considered as being less interesting here. Application of silicon technology is preferred because it is the most common fabrication technique in the field of microtechnology.

In the introduction, figure 1.1 showed the three-axis approach of categorizing sensors. The used technology, the measured parameter and the measuring electronic device were chosen to be placed on the three axis, which was a logical result of a certain generalization of sensors. This idea of displaying these items in a three dimensional graph is rather deceptive because the classifications do not contain information which can be placed on a linear scale.
Figure 6.1 shows a two-axis graph of sensors categorized on their used technology and the measured parameter.

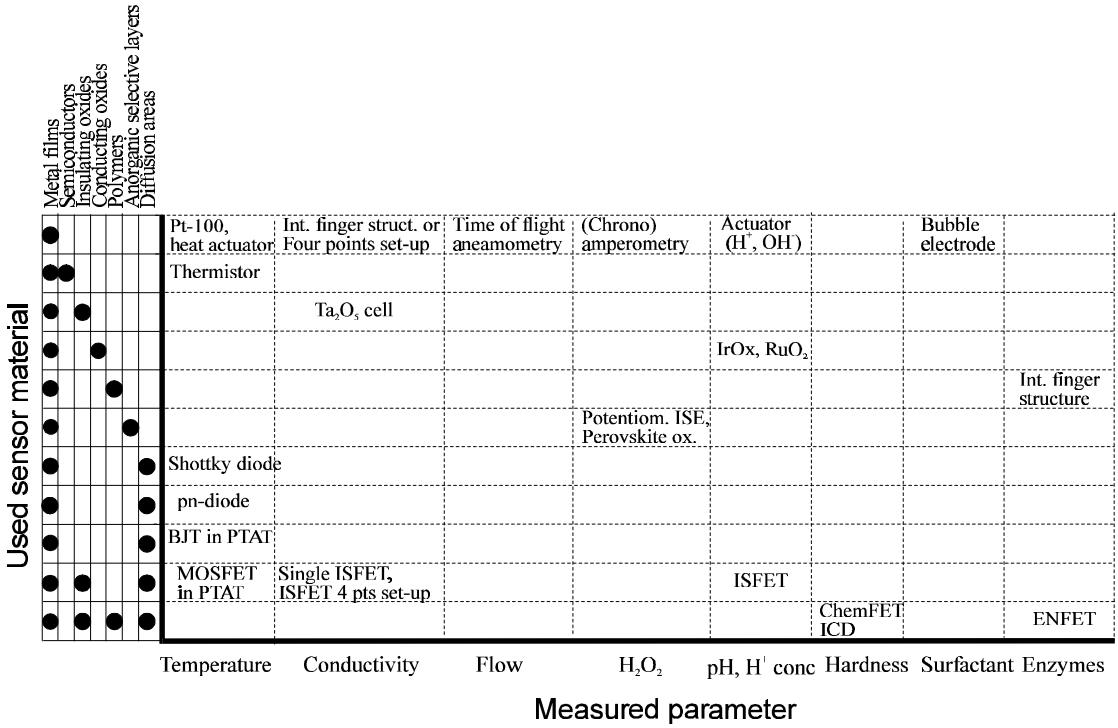


Fig. 6.1: Sensors categorized on their materials and parameters

When chosing the implementation of the sensor array according to the used fabrication technique, some remarks can be made from this graph.

6.1. Realization of the sensor array using metal films only

The first conclusion from figure 6.1 can be that with only using deposited and patterned metal layers, a wide variety of physical and chemical parameters can be measured already. The metals meant here are chemically inert ones like platinum and gold. Only the measurement of hardness and pH using metal films only was not reported in literature, but a more exhaustive search can be performed when this technology is chosen for the fabrication of the sensor array.

From the first row of figure 6.1 and recalling section 4.1. it can be seen that the following washing parameters can be obtained using only metal layers:

Table 6.1: Washing parameters that can be measured using metal films only

Washing parameter	Description	Used sensors
Water quality	The conductivity measured in the tap water gives information about the water quality.	Interdigitated finger structure or four points conductivity set-up
Amount of soil	An impression can be obtained by evaluating the conductivity of the water in the tub before washing.	Same as above
Rinsing effectiveness, turbidity	For rinsing effectiveness, conductivity might be a good indicator.	Same as above
Temperature	The thermoresistive effect of platinum gives a reliable temperature measurement.	Pt-100 sensor
Bleach activity	Electrochemical detection of hydrogen peroxide seems possible	Chrono-amperometric sensor
Surfactant monitoring	Making use of the relation between dynamic surface tension and surfactant concentration. (Technology requires actually an anisotropic etch of silicon)	Bubble electrode

Although this gives a rather complete impression of a washing process, important parameters like hardness and pH are missing.

6.2. Realization of the sensor array using oxidation technology

When the parameters that are missing in the metal-film-only approach seem to be very important to the process monitoring, or when the needed accuracy cannot be obtained it can be considered to expand the technology with oxidation steps. The used technology is then still simple (deposition technology only).
The first advantage is that the insulating oxide Ta_2O_5 has some possibilities of improving conductivity measurements. Furthermore, with iridium oxide and ruthenium oxide a new parameter can be obtained: pH. Besides the direct interest of

measuring pH, some systems were reported were the sensing of pH is part of a combined sensor-actuator system.

6.3. Realization of the sensor array using ISFETs

One big advantage is that an ISFET can be used in combination with a H^+/OH^- actuator. It can be stated from measurement technology considerations that the only way to build a sensor with a decent reference system and which has the possibility of auto calibration, is in combination with an actuator. The demands on the sensor are then transformed to demands on the actuator.
Since the possibilities of ISFETs and metal oxide based pH sensors are theoretically equal, the best choice cannot be made at this moment. In the development stage, probably all pH sensing will be done using ISFETs because of the experiences in the biosensor group.

6.4. Future work

Now a global tendency towards metal film-only sensors is concluded, the next step will be that of an analysis of the feasibility of such sensors. This is necessary because this report does not say anything about the possibilities of the given standard sensors in washing system.
The feasibility analysis can be done by choosing a sensor and doing some measurements. The measurement of bleach activity (hydrogen peroxide concentration) using chrono-amperometry is already started, together with a more exhaustive search for water hardness measurements.

7. Index

H

I

L

M

N

O

P

Q

R

S

T

U

V

Z

8. References

[1] Webster, Medical instrumentation systems, application and design, Houghton Mifflin Company, Boston, 1992

[2] J.H. Fluitman, A. van den Berg and T.S Lammerink, Micromechanical components for µTAS, Proc. Micro total analysis sytems, page 73-83, Kluwer academic publishers, 1995

[3] A. Dittmar, H. Rada, G. Delhomme, E. Vernet-Maury, C. Collet, R. Roure, R. Unterreiner, M. Robini, C. Delemer, A multi-sensor system for the non-invasive measurement of the activity of the autonomic nervous system, Sensors and Actuators B 26-27 (1995), page 461-464

[4] S. Middelhoek and S. Audet, Silicon sensors, microelectronics and signal processing, Academic Press Limited, London, 1989

[5] J.F.J. Engbersen, W. Olthuis and M. Bos, Chemical micro-sensors, The principles of chemical selection, transduction and signal processing, MESA course, 1995

[6] Karl-Dittmar Klein, Voltage relaxations of bi-electrodes for the long term monitoring of concentrations of hydrogen peroxide, glucose, etc., Sensors and Actuators B 22 (1994) page 127-132

[7] Richard S.C. Cobbold, Transducers for biomedical measurements: principles and applications, John Wiley & sons, New York, 1974

[8] Allen J. Bard and Larry R. Faulkner, Electrochemical methods: fundamentals and applications, John Wiley & sons, New York, 1980

[9] R.W. Murray, Chronoamperometry, chronocoulometry and chronopotentiometry, From: B.W. Rossiter, J.F. Hamilton, Physical methods of chemistry, 2nd edition, volume II, 1986, page 525 - 589

[10] A. Volanschi, W. Olthuis, P. Bergveld, Gas bubbles electrolytically generated at microcavity electrodes (MCE) used for the measurement of dynamic surface tension in liquids, Proc. Transducers '95, Eurosensors IX, June 25-29 1995, Sweden

[11] S. Roy Morrison, Electrochemistry at semiconductor and oxidized metal electrodes, Plenum press, New York, 1980

[12] Marc J. Madou and S. Roy Morrison, Chemical Sensing with solid state devices, Academic Press, Inc., 1989

[13] W. Olthuis, A. Volanschi, J.G. Bomer and P. Bergveld, A new probe for measuring electrolytic conductance, Sensors and Actuators B, 13-14 (1993), page 230-233

[14] M. Lambrechts and W. Sansen, Biosensors: bioelectrochemical sensors, IOP Publishing,1992

[15] K.G. Kreider, M.J. Tarlov, J.P. Cline, Sputtered thin film pH electrodes of platinum, palladium, ruthenium, and iridium oxides, Sensors and Actuators B 28 (1995), page 167-172

[16] W. Olthuis, Iridium oxide based coulometric sensor-actuator systems, thesis University of Twente, 1990

[17] Gábor Harsányi, Polymeric sensing films: new horizons in sensorics?, Sensors and Actuators A, 46-47 (1995), page 85-88

[18] J.W. Thackeray and M.S. Wrighton, Chemically responsive microelectrochemical devices based on platinized poly(3-methylthiophene): variation in

conductivity with variation in hydrogen, oxygen, or pH in aquous solution, J. Phys. Chem. 1986, 90, page 6674-6679
[19] T. Shimidzu, Derivation of conducting polymers with functional molecules directed via molecular structural control towards a molecular device, Reactive polymers, 11 (1989), page 177-189
[20] P. Burgmayer and Royce W. Murray, Ion gate electrodes, polypyrrole as a witchable ion conductor membrane, J. Phys. Chem. 1984, 88, page 2515-2521
[21] A.A. Saaman and P. Bergveld, A classification of chemically sensitive semiconductor devices, Sensors and Actuators, 7 (1985), page 75 - 87
[22] I. Lundström, Hydrogen sensitive MOS-structures, Part 1: principles and applications, Sensors and Actuators, 1 (1981), page 403 - 426
[23] I. Lauks, Polarizable electrodes, Part II, Sensors and Actuators, 1 (1981) page 393 - 402
[24] A. Volanschi, W. Olthuis and P. Bergveld, Electrolyte conductivity measured with an ISFET, Proceedings conf. Trends in electrochemical biosensors, Trieste, Italy, June 1992
[25] A. Volanschi, W. Olthuis and P. Bergveld, Design of a miniature electrolyte conductivity probe using ISFETs in a four point configuration, Sensors and Actuators B, 18-19 (1994) page 404-407
[26] J. Holleman and J.B. Rem, Thin film transistors for matrix sensors and actuators, Proceedings of the 2nd international workshop on materials science (IWOMS'95), Hanoi, Oct. 1995
[27] P. Bergveld, Chemically sensitive electronic devices, microanalysis and microelectronics, Proc. of the 2nd int. meeting on chemical sensors, Bordeaux, 1986
[28] Y.G. Vlasov, E.A. Bychkov and A.V. Legin, Mechanism studies on lead ion-selective chalcogenide glass sensors, Sensors and Actuators B, 10 (1992), page 55 - 60
[29] Datahandbook Philips Semiconductors, Semiconductor sensors, book SC17, 1995
[30] Y. Shimizu, H. Komatsu, S. Michishita, N. Miura and N. Yamazoe, Hydrogen peroxide sensor based on carbon electrode loaded with perovskite-type oxide, Proceedings of Transducers '95, Eurosensors IX, page 981-984, Stockholm, Sweden, June 1995
[31] R.S. Muller, Heat and strain sensitive thin film transducers, Sensors and actuators, 4 (1983), page 173 - 182
[32] P.W. Atkins, Phisical Chemistry, fifth edition, Oxford university press, 1994
[33] A.I. Vogel, Vogel's textbook of qualitative inorganic materials, 4th edition, Longman Group Ltd., London 1978
[34] H.N. Norton, Electronic analysis instruments, Prentice Hall Inc., New Jersey 1992
[35] D.A. Skoog and D.M.West, Analytical Chemistry, Saunders golden sunburst series, Philadelphia, 1980
[36] P. Bergveld, The impact of MOSFET-based sensors, Sensors and Actuators, 8 (1985), page 109 - 127
[37] R. van Hal, Advanced packaging of ISFETs, design, encapsulation and bonding, thesis University of Twente, 1994

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