Development of high temperature SiC based field effect sensors for internal combustion engine exhaust gas monitoring

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While the car fleet becomes increasingly larger it is important to lower the amounts of pollutants from each individual diesel or gasoline engine to almost zero levels. The pollutants from these engines predominantly originate from high NO\textsubscript{x} emissions and particulates, in the case when diesel is utilized, and emissions at cold start from gasoline engines.

One way of treating the high NO\textsubscript{x} levels is to introduce ammonia in the diesel exhausts and let it react with the NO\textsubscript{x} to form nitrogen gas and water, which is called SCR (Selective Catalytic Reduction). However, in order to make this system reduce NO\textsubscript{x} efficiently enough for meeting future legislations, closed loop control is required. To realize this type of system an NO\textsubscript{x} or ammonia sensor is needed.

The cold start emissions from gasoline vehicles are primarily due to a high light-off time for the catalytic converter. Another reason is the inability to quickly heat the sensor used for controlling the air-to-fuel ratio in the exhausts, also called the lambda value, which is required to be in a particular range for the catalytic converter to work properly. This problem may be solved utilizing another, more robust sensor for this purpose.

This thesis presents the efforts made to test the SiC-based field effect transistor (SiC-FET) sensor technology both as an ammonia sensor for SCR systems and as a cold start lambda sensor. The SiC-FET sensor has been shown to be highly sensitive to ammonia both in laboratory and engine measurements. As a lambda sensor it has proven to be both sensitive and selective, and its properties have been studied in lambda stairs both in engine exhausts and in the laboratory. The influence of metal gate restructuring on the linearity of the sensor has also been investigated. The speed of response for both sensor types has been found to be fast enough for closed loop control in each application.
# Table of contents

ABSTRACT ................................................................................................................................. 1  
LIST OF PAPERS....................................................................................................................... 5  
ACKNOWLEDGEMENTS .......................................................................................................... 7  
1. INTRODUCTION .................................................................................................................. 9  
   1.1. ENVIRONMENTAL ASPECT OF EXHAUST GAS CLEANING ....................... 9  
   1.2. GASOLINE EXHAUST CLEANING ..................................................................... 10  
   1.3. DIESEL EXHAUST CLEANING ......................................................................... 11  
   1.4. ALTERNATIVE FUELS ..................................................................................... 11  
   1.5. THE SCOPE OF THE THESIS ........................................................................ 14  
2. THE INTERNAL COMBUSTION ENGINE .......................................................................... 15  
   2.1. THE ENGINE SYSTEM ..................................................................................... 15  
   2.2. THE FOUR STROKE CYCLE ........................................................................... 16  
   2.3. EXHAUST GAS AFTER TREATMENT ................................................................... 18  
   2.4. THE DIFFERENCE BETWEEN GASOLINE AND DIESEL ENGINES ....... 18  
3. THE COMPOSITION OF EXHAUST GASES .................................................................... 20  
4. CLEANING OF THE EXHAUST GASES .......................................................................... 22  
5. GASOLINE ENGINES: MEASURING THE LAMBDA VALUE ........................................ 25  
   5.1. THE METAL OXIDE SENSOR ............................................................................. 26  
      5.1.1. The sensing principle of metal oxide sensors (MOS) ......................... 26  
      5.1.2. The binary zirconia sensor ................................................................. 30  
      5.1.3. The linear zirconia sensor ................................................................. 31  
      5.1.4. The titanium oxide sensor ............................................................... 32  
   5.2. THE FIELD EFFECT TRANSISTOR SENSOR ................................................. 33  
      5.2.1. Sensor principle .................................................................................. 33  
      5.2.2. The SiC-FET lambda sensor ............................................................. 38
6. DIESEL ENGINES: MEASURING AMMONIA SLIP .......... 40
  6.1. THE ZEOLITE-BASED SENSOR ................................................... 42
  6.2. THE MIXED-POTENTIAL ZIRCONIA SENSOR ............................... 43
  6.3. THE MOLYBDENUM OXIDE SENSOR ........................................ 43
  6.4. THE SiC-FET SENSOR ............................................................ 44

7. THE SiC FIELD EFFECT DEVICE ........................................ 45
  7.1. THE PROPERTIES OF SiC ........................................................... 45
  7.2. THE DIFFERENT TYPES OF FIELD EFFECT SENSORS ................... 46
  7.3. THE SiC CAPACITOR ............................................................... 48
  7.4. THE SiC SCHOTTKY DIODE .................................................... 51

8. THE SENSITIVE LAYER .......................................................... 53
  8.1. THE CATALYTIC GATE MATERIALS AND THEIR PROPERTIES ....... 53
  8.2. SPITTER DEPOSITION ............................................................... 55
  8.3. EVAPORATION ........................................................................ 56
  8.4. LONG-TERM STABILITY .......................................................... 57

9. METHODS .................................................................................... 59
  9.1. PRODUCTION AND MOUNTING .................................................. 59
  9.2. LAMBDA SENSOR FOR CLOSED LOOP CONTROL ..................... 62
  9.3. AMMONIA SENSOR FOR SCR SYSTEMS .................................. 63

10. RESULTS .................................................................................... 65
  10.1. LAMBDA SENSOR FOR CLOSED LOOP CONTROL .................... 65
  10.2. AMMONIA SENSOR FOR SCR SYSTEMS .................................. 66

11. FUTURE WORK ........................................................................... 68

12. REFERENCES ............................................................................... 70
List of papers

This licentiate thesis is based on the following papers:


Related papers, not included in this licentiate thesis:


My contribution to the papers included in this thesis:

Paper I: All experimental work, data evaluation and writing
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1. Introduction

1.1. Environmental aspect of exhaust gas cleaning

Most engines in the car fleet today are either gasoline or diesel driven. There are some vehicles that utilize alternative energy sources - such as methanol, bio fuel, hydrogen or electricity from batteries - but the penetration of these in the society has for several reasons been difficult to achieve.

One of the major problems with using fossil fuels as an energy source, and which works as a driving force for developing other means of attaining power, is the high amount of pollutants emitted from engines utilizing such fuels. The levels of pollutants have been significantly reduced since the introduction of the catalytic converter in the 1980s. However, whereas the number of cars throughout the world steadily rises, it becomes increasingly important to find means to maintain an environment, especially in large cities, that is pleasant to live in. As a consequence of this the legislations concerning allowed levels of pollutants from cars and trucks constantly becomes stricter. The emissions of nitrogen oxides, for example, have to be reduced with another factor of 10 within the next five years. The main problem areas concerning emissions can be found during cold start, in the case with gasoline engines, and in the high nitrogen oxides and particulate emissions from diesel driven vehicles. In order to make the emissions from gasoline and diesel engines pass the restrictive legislations concerning pollutants these problems need to be solved.
1. Introduction

1.2. Gasoline exhaust cleaning

The cleaning of the exhausts from gasoline engines mainly depends on the ability of the catalytic converter to combust species such as hydrocarbons, carbon monoxide and nitrogen oxides. The efficiency of the three-way - three different species are treated - catalytic converter when oxidizing and reducing these pollutants to less harmful species is determined by the air-to-fuel ratio in the exhausts. The air-to-fuel ratio is measured in terms of the lambda value, denoted with the symbol $\lambda$, which is one at stoichiometric conditions. The lambda value is defined as the air-to-fuel mass ratio in the engine exhausts divided by the air-to-fuel mass ratio at stoichiometric conditions (Eq. (1)). At a lambda value above one the fuel mixture is said to be lean and below one it is called rich.

$$
\lambda = \frac{(m_{air}/m_{fuel})_{engine}}{(m_{air}/m_{fuel})_{stoich}}
$$

The conversion of pollutants requires a lambda value close to one, that is, there should be such a concentration of hydrocarbons, carbon monoxide and nitrogen oxides that only water, carbon dioxide and nitrogen are produced after they have been allowed to react with each other. Since it is not so easy to predict the lambda value from measured engine parameters it needs to be regulated through closed loop control. This involves the use of a lambda sensor, which measures the air-to-fuel ratio in the exhausts and is used for regulating the amount of air that is added to the fuel. At cold start, however, there are two major problems with this cleaning system. First of all, the catalytic converter cannot easily be heated to its operating temperature of about 250-300ºC. This means that the conversion of harmful species cannot take place. This is the main reason why most of the total emissions from a gasoline engine during a driving cycle are let out into the environment during the first few minutes after the engine has been started. Secondly, there is also a
problem with the lambda sensor that controls the air-to-fuel ratio of the exhausts that reach the catalytic converter. When the engine is cold, water vapor from the combustion of the fuel condense and form droplets on the walls of the exhaust pipe. These droplets are carried downstream with the exhaust flow. If the droplets hit the fragile lambda sensor while it is heated to its operating temperature of 650-750ºC it may break. To avoid this the lambda sensor is not fully heated until the exhaust system is sufficiently warm and thus the efficiency of the catalytic converter is not optimal during this time. It should be noted that the methods to heat up the catalytic converter faster are under development, but even if it is sufficiently heated within ten seconds or less the problem with the brittle lambda sensor still remains.

### 1.3. Diesel exhaust cleaning

The emissions from diesel engines cannot be reduced as easily as by using a three-way catalytic converter. This is because the combustion of diesel occurs with air in excess, which gives a lambda value that is much higher than one. Hydrocarbons and carbon monoxide can still be converted into carbon dioxide and water if a catalytic converter is used, but the reduction of nitrogen oxides is not catalytically favored. Thus, the amounts of nitrogen oxides from a diesel engine are very high, which is the major drawback of the diesel engine in comparison with its gasoline counterpart.

### 1.4. Alternative fuels

Another problem with gasoline and diesel engines is that they have an intrinsic property of producing a high amount of carbon dioxide. Since carbon dioxide is a green house gas it is desirable to lower these emissions considerably in the future. The efficiency of the combustion of diesel is higher than for gasoline, which means that the carbon dioxide
produced per energy unit is higher for gasoline than for diesel. This is one advantage of the diesel engine that makes it attractive among car manufacturers today. Much research is therefore devoted to solving the problems of nitrogen oxides and particulate emissions from these engines. The goal is to replace the gasoline engine in modern cars and make the already existing diesel engines meet the coming legislations on emissions.

However, even if the engines fuelled with gasoline or diesel are made as environmentally attractive as they can possibly be, there are still several reasons for developing energy sources that are not based on the use of fossil fuels. Even if the carbon dioxide emissions are cut to a minimum by using highly effective diesel engines there will still be a considerable amount of the gas let out into the environment. The car fleet is expected to expand more and more as a larger number of countries become well-developed, and even if the emissions from a single vehicle is close to negligible the total emissions from the entire car fleet are still significant. Moreover, it is unclear for how long the oil reservoirs may last, which certainly creates a reason for developing engines that are based on another energy source than fossil fuels.

One alternative is to use bio fuel or methanol instead of fossil fuels. The benefits of these fuels are, among others, that they can easily be produced, can be used in the same type of engine as we have today and can be distributed to customers via the same system as gasoline and diesel. An argument against the use of these fuels is that they do not solve the problems with emissions of carbon dioxide. On the other hand they are made from carbon sources already existing in the ecological system and do not add any new amounts of carbon dioxide to the air.

Another possibility is to utilize an energy source that does not in itself produce any harmful emissions, such as hydrogen. When extracting energy from hydrogen, e.g. in a fuel cell, the hydrogen gas is oxidized by
air and form pure water. This may very well seem like the perfect fuel with regard to emissions. However, there are presently many serious drawbacks connected to this type of energy source. First of all, the production of hydrogen today is both expensive and in many cases environmentally harmful. The cost benefit with using fossil fuels instead of hydrogen could perhaps be overcome by tax regulations and governmental laws. The other disadvantage of hydrogen production is more difficult to change, since new, highly efficient methods for producing hydrogen need to be developed. It is a common opinion that the use of hydrogen does not give zero emission vehicles but rather "displaced emission vehicles", and that using hydrogen as an energy source does not solve any environmental problems. Another large problem with hydrogen as a fuel is how it should be stored before combustion. There are many suggestions on how to store the hydrogen, such as compressed, cooled to liquid form or as a metal hydride, but the storage is in such cases either too ineffective with regard to energy per weight, or requires a cooling equipment which in itself consumes a considerable amount of energy [1]. Moreover, there is no distribution network for hydrogen today. This problem could be avoided by producing the hydrogen either at the gas stations or in the car, even though these possibilities are clearly equipped with other potential obstacles.

In conclusion, one could say that there are many alternative fuels to gasoline and diesel, but as it is today the technology for producing, distributing and storing the fuel is either too expensive or not mature. The benefits of oil-based fuels are that their production is inexpensive and that they are easily distributed to customers through a well-developed system of pipelines and tank stations. Moreover, the energy content per kilo fossil fuel is high, which makes the storage volume and weight fairly low and the time between required filling stops quite long. This means that until a more competitive energy source is on the market
1. Introduction

the main objective is to enhance the diesel or gasoline exhaust gas cleaning systems.

1.5. The scope of the thesis

In this thesis the development of sensors that could help solving the problems with present engine emissions is discussed. The research has been performed in two different applications; developing a lambda sensor for cold start closed loop control and an ammonia sensor for use in systems where selective catalytic reduction (SCR) of nitrogen oxides takes place by introducing urea in the system. This thesis gives some introductory information on the engine and its emissions together with a detailed description of the applications. The SiC field effect sensor, which is the focus of the research, will be thoroughly described together with other competing sensor technologies. The results obtained this far together with some suggestions on future work are presented in the last chapters of the thesis.
2. The internal combustion engine

In this section the most basic principles concerning the internal combustion engine are described. The details treated have been chosen according to what is most significant for the research presented in this thesis, such as where the emissions are produced, what the lambda value is and how it can be regulated in order to get an efficient conversion of the pollutants in the catalytic converter.

2.1. The engine system

A simplified picture of a gasoline internal combustion engine can be said to consist of six different parts; the throttle, the fuel injector, the intake manifold, the cylinder, the exhaust manifold and the catalytic converter. A schematic picture of this system is shown in Fig. 1. The fundamental process that takes place in the engine is the combustion of a mixture of fuel and air and the following production of crankshaft momentum and emissions.

The air is taken in through the throttle, which is a butterfly valve that allows the airflow to be changed in a continuous way. The butterfly valve is usually connected to the accelerator, which means that the driver determines the amount of air that is taken in. The air that passes the throttle enters the intake manifold at a rate that is determined by the speed of the engine. The fuel is injected at the end of the intake manifold, close to the cylinder, where it vaporizes and is mixed with the air. The fuel mixture is then carried to the cylinder and combusted, which results both in the release of energy and the formation of emission species. A large part of the energy - as much as 50-55% in the case of a gasoline engine [2] - is then let out from the cylinder together with the exhausts in the form of heat, while the rest is used for running the
2. The internal combustion engine

vehicle. Before the exhausts are exiting the engine system they pass the catalytic converter, where most of the environmentally harmful species are taken care of.

Fig. 1. The engine consists of the throttle, the intake manifold, the cylinder, the exhaust manifold and the catalytic converter [2].

2.2. The four stroke cycle

The most central part in the internal combustion engine is the cylinder, which is where the combustion of gasoline or diesel takes place. This is also where the energy released in the combustion process is transferred to the rest of the vehicle and where all the emissions are produced. The cylinder mainly consists of a cylinder-shaped volume in which a piston is placed. The piston is allowed to move back and forth and thereby change the volume of the cylinder. A schematic drawing of the cylinder is shown in Fig. 2. There are two openings shown at the top of the cylinder ((3) and (4)). One of them is for air and fuel intake and the other
2. The internal combustion engine

one for exhaust outlet. These are opened and closed with two individual valves. The piston is connected to the crankshaft (5) through a rod.

Fig. 2. A schematic drawing of the (1) cylinder, (2) piston, (3) intake valve, (4) exhaust valve and (5) crankshaft.

During combustion the cylinder is working in a four stroke cycle. This means that four different working conditions can be identified. In the first of these the piston moves from its highest to its lowest position while a mixture of fuel and air is introduced through the opened inlet valve. The movement of the piston is either induced by the starting motor or by the speed of the crankshaft from a previous cycle. Following this is the closure of the valve and the compression of the fuel and air gas mixture by the piston that now moves upwards. Slightly
before the piston starts moving downwards again the fuel is ignited and combustion takes place. This adds extra energy to the downward movement of the piston and thereby also to the crankshaft. Finally the piston moves to its highest position again, while the exhausts are let out through the exhaust valve, and the cylinder is ready for another four stroke cycle.

### 2.3. Exhaust gas after treatment

The number of cylinders of an internal combustion engine depends on the desired power output. The exhausts from all cylinders join in the manifold, and are carried through the exhaust pipe. Closely after the manifold is the catalytic converter. When passing through the catalytic converter harmful species such as nitrogen oxides, hydrocarbons and carbon monoxide are reduced or oxidized into nitrogen gas, water and carbon dioxide. As mentioned in the introduction the catalytic converter requires an air-to-fuel ratio close to one in order to work efficiently. Therefore, a sensor is placed before the catalytic converter which measures the air-to-fuel ratio. The signal from the sensor is usually connected to the fuel injector of the engine via closed loop control. If the air-to-fuel ratio deviates from stoichiometry the settings for the fuel injector are changed so that a close to stoichiometric air-to-fuel ratio is achieved again.

### 2.4. The difference between gasoline and diesel engines

The gasoline and diesel engines are both of internal combustion type, but there are also many differences between the engines. Diesel fuel, which contains longer carbon chains compared with gasoline, enters the engine system from an injector placed inside the cylinder. The combustion follow a four-stroke cycle, as described in section 2.2, but when the inlet valve opens and the cylinder volume is increased only air
is introduced in the cylinder. The inlet valve is then closed and the air is compressed. At the end of the compression fuel is injected. At this point the air is already warm due to the compression, and when the fuel enters the cylinder it self-ignites. The remaining parts of the four-stroke cycle are similar to the case when gasoline is used.

The engine system shown in Fig. 1 is typical for a gasoline engine. The diesel engine utilizes a similar system, but it does not have a throttle. Also, the combustion takes place with air in excess, which gives a lambda value of the exhausts that is far from stoichiometry. This means that the same type of catalytic converter as in gasoline engines cannot be used. Moreover, the compression of the fuel mixture can be made larger than for the gasoline engine, which gives a higher fuel efficiency.
3. The composition of exhaust gases

In the combustion of the fuel in the cylinders of a gasoline or diesel engine, many different gases are produced. Carbon monoxide, carbon dioxide and water are formed when the hydrocarbons are combusted. There are also hydrocarbons from the incomplete combustion of the fuel in the exhausts. The hydrocarbons are of many different types and most of them are unsaturated. Nitrogen oxides originate from the reaction between oxygen and nitrogen molecules that are present in the air that is added to the fuel. The energy that is required for this reaction to occur is taken from the combustion of the fuel. There may also be small amounts of sulphur dioxide and phosphorus in the exhausts, due to impurities in the fuel.

Fig. 3. The composition of exhaust gases from a diesel engine at different lambda values [2].
3. The composition of exhaust gases

The exact composition of the exhausts depends on the type of fuel used, together with the load of the engine and the amount of air that is added to the fuel at the combustion. The composition of exhaust gases from a gasoline engine at different lambda values are shown in Fig. 3.

Many of the gases present in the exhausts are harmful, either to the environment or as health hazards. The three gases that are most harmful are hydrocarbons, carbon monoxide and nitrogen oxides. Hydrocarbons and nitrogen oxides cause smog, and nitrogen oxides are also a cause of acid rain. Carbon monoxide is very poisonous and has a suffocating effect on humans. Due to this, it is of general interest to diminish the concentrations of these gases in the exhausts. The legislations concerning the emissions become stricter and stricter, and will reach almost zero levels for both gasoline and diesel vehicles in a near future [3, 4]. A considerable amount of these gases is successfully converted to more harmless species by using a catalytic converter. The present conversion efficiency of the catalytic converter throughout the entire driving cycle when being used in either gasoline or diesel engines is, however, not enough for meeting the strict legislations. Much of the present research on decreasing the pollutants is therefore devoted to increasing the efficiency of the catalytic converter, either by using new materials, achieving a faster warm-up or optimising the conditions for conversion to take place, or by designing alternative exhaust gas after treatment systems.
4. Cleaning of the exhaust gases

In all modern gasoline cars today there is a three-way catalytic converter, placed somewhere between the exhaust manifold and the muffler. The denotation "three-way" means that mainly three different species are converted, that is hydrocarbons, carbon monoxide and nitrogen oxides.

The catalytic converter consists of a honeycomb structure coated with metal oxides and impregnated with catalytic metals, for example platinum, palladium and rhodium. The catalytic metals facilitate the conversion of the three above-mentioned species into less harmful gases, like nitrogen, oxygen, carbon dioxide and water.

![Fig. 4. The efficiency of the catalytic converter when converting hydrocarbons, CO and NO\textsubscript{x} reaches its optimum value for a lambda value close to one, or when the air-to-fuel mass ratio is 14.7.](image)

As mentioned previously, one requirement of the catalytic converter in order to work properly is that the gas mixture that leaves the cylinders has the right composition. It is important that the exhausts are very close to stoichiometry for the cylinder to work efficiently. This means that the
4. Cleaning of the exhaust gases

lambda value should be close to one. Lambda is equal to one when the mass ratio between air and fuel in the exhausts is 14.7 (Fig. 4). The lambda value is dependent on the concentrations of several exhaust gas species, and close to stoichiometry it can be calculated according to Eq. (2), with concentrations in percent.

$$\lambda = 1 + \left( \frac{[O_2] + \frac{1}{2}[NO] + \frac{1}{2}[CO] - (x + \frac{y}{4})[C,H_y] - \frac{1}{2}[H_2]}{20} \right)$$  \hspace{1cm} (2)

Mainly the reactions given in Eq. (3) - (7) occur in the catalytic converter [5].

$$C,H_y + (x + \frac{y}{4})O_2 \rightarrow xCO_2 + \frac{y}{2}H_2O$$  \hspace{1cm} (3)

$$CO + \frac{1}{2}O_2 \rightarrow CO_2$$  \hspace{1cm} (4)

$$NO + CO \rightarrow \frac{1}{2}N_2 + CO_2$$  \hspace{1cm} (5)

$$NO + H_2 \rightarrow \frac{1}{2}N_2 + H_2O$$  \hspace{1cm} (6)

$$(2 + \frac{y}{2})NO + C,H_y \rightarrow (1 + \frac{y}{4})N_2 + xCO_2 + \frac{y}{2}H_2O$$  \hspace{1cm} (7)

These reactions are unfortunately not the only ones that take place in the catalytic converter. There are also a certain amount of nitrous oxide, also known as laughing gas, and ammonia produced, according to Eq. (8) - (11) [5].

$$2NO + 5CO + 3H_2O \rightarrow 2NH_3 + 5CO_2$$  \hspace{1cm} (8)
4. Cleaning of the exhaust gases

\[ 2NO + 5H_2 \rightarrow 2NH_3 + 2H_2O \] \hspace{1cm} (9)

\[ 2NO + CO \rightarrow N_2O + CO_2 \] \hspace{1cm} (10)

\[ 2NO + H_2 \rightarrow N_2O + H_2O \] \hspace{1cm} (11)

These two gases are harmful, both to the environment like nitrous oxide, since it is a greenhouse gas, and to organisms like ammonia. It is claimed that especially the production of nitrous oxide is a serious problem, and that much of the nitrous oxide that is exhausted to the atmosphere actually comes from cars with catalytic converters [6]. The problem with the production of nitrous oxide is assumed to originate from reactions taking place when the catalytic converter is not fully heated. Thus, this is yet another problem at cold start that adds to the ones mentioned earlier.

In a diesel engine the three-way catalytic converter cannot be used. The reason for this is that the lambda value is above one in diesel exhausts, which is too high for the three-way catalytic converter to be effective. Instead a special catalytic converter is used, in which only oxidizing reactions occur. This means that only hydrocarbons and carbon monoxide can be converted, while the high amounts of nitrogen oxides are let out in the environment. This problem may be dealt with by using other methods, such as adding ammonia to the exhausts, as is further described below.
5. Gasoline engines: Measuring the lambda value

As has been mentioned earlier, the lambda value is a measure of how close the gas mixture that reaches the catalytic converter is to stoichiometry. In the introduction a definition of the lambda value was given, and it was declared that at stoichiometry the lambda value is equal to one. In order to get an efficient conversion of harmless species in the catalytic converter the lambda value needs to be kept close to stoichiometry. This is achieved by regulating the lambda value by closed loop control through adjusting the mixture of air and fuel in the cylinders. This means that the lambda value needs to be measured after the combustion of the fuel, so that a decision can be made about how to mix the air and the fuel.

The regulation is kept in a self-oscillating mode, which means that the lambda value will fluctuate around a value of one. This oscillation increases the durability of the catalytic converter and also facilitates the reactions taking place on the catalytic surface.

There are also other places in the exhaust pipe than before the catalytic converter where it is valuable to measure lambda, e.g. after the catalytic converter. The purpose of this measurement is to check whether the catalytic converter is functioning normally or not. If the lambda value after the catalytic converter is the same as before the catalytic converter it indicates that the after treatment system is not working properly.

Even though regulation of lambda takes place, the exhaust gas composition may vary a lot during a driving cycle. The lambda value is usually in the interval 0.99-1.05, but in rare cases it can be as low as 0.75.

According to Volvo Technology such a cold start lambda sensor should, except for being thermo shock resistant, be selective and sensitive to
5. Gasoline engines: Measuring the lambda value

lambda in proximity of the stoichiometric ratio. It should also have a
time to operation of $< 5$ s, a response time of $< 10$ ms and a long-term
stability for 240 000 km.

When the fuel mixture changes from being lean to rich, or the opposite,
a significant change occurs in the exhaust gas composition. This change
can be measured by different types of sensors and then related to the
lambda value. There are many sensor types that can be used, for example
the yttria-stabilised zirconia sensor, the titanium oxide MOS sensor and
the SiC field effect sensor. The zirconia sensor technology is presently
used as a lambda sensor in modern cars but cannot be heated to its
operating temperature directly after cold start. The reason is that during
cold start water droplets are formed in the exhaust pipe that may be
carried downstream to the heated lambda sensor and break it. To avoid
this, another one of the sensor types may be used for measuring the
lambda value at cold start. One of the scopes of this thesis is to develop
a cold start lambda sensor based on the SiC-FET technology. The
technologies behind this sensor as well as the other types are treated in
the following sections.

5.1. The metal oxide sensor

5.1.1. The sensing principle of metal oxide sensors (MOS)

The metal oxide sensor consists of a wide-bandgap semiconducting
material such as ZnO, SnO$_2$ or ZrO$_2$. The conductivity of this material is
usually chosen as the sensor signal, although the sensor may very well
also be based on a capacitor or a Schottky diode. The latter is especially
used for characterizing the sensor properties. Measuring the conductivity
gives the largest change in sensor signal, which is the main reason why
this mode of operation is the most frequent choice. [7, 8]
The semiconductor is in most practical cases a polycrystalline film, which is made up of a great amount of small grains. When these grains get into contact with gas molecules, such as oxygen or hydrogen, the molecules adsorb on the surface (Fig. 5). Three different temperature regions affect the continuing behavior of the semi-conducting film. [7-9]

![Fig. 5. When oxygen molecules adsorb at the grain boundaries, a space-charge region is induced.](image)

At medium temperatures, below 700ºC, the oxidizing molecules from the gas accept electrons from the material, which causes a region to form close to the surface where the density of electrons is lower than in the bulk. This is called a space-charge region. Adding molecules from reducing species, on the other hand, makes the electron concentration at the surface higher than inside of the material. [7, 8]

The concentration of electrons at the grain boundaries has a great influence on the overall conductivity of the material, at least at these rather low temperatures. The removal of electrons gives a higher resistance between the grains than within them, which creates electron barriers between the grains and causes an increase of the overall resistance. This means that the conductivity will give much information on whether the ambient atmosphere of the sensor is oxidizing or reducing. When the semiconductor is exposed to oxygen, it will dissociate on the surface and accept two electrons from the material,
which gives a low conductivity. The most frequent case is that hydrogen or CO or hydrocarbons then react with the adsorbed oxygen. The oxidized reaction species leave the surface while the electrons that formerly belonged to oxygen are returned to the grain and the conductivity is increased. The change in the sensor signal when going from an oxidizing atmosphere of one to another oxygen concentration is the sensor response. [7, 8]

At temperatures above 700ºC the conductivity of the bulk in some materials will be of greater importance than the surface effects. Then ions will be transported through lattice defects inside of the material, and thereby give rise to an ion current. An equilibrium situation between the gas molecules and the lattice defects will be reached. If two sides of the material are attached to electrodes and exposed to different gas mixtures, there will be a potential difference between the two electrodes. This potential difference can be described by the Nernst equation, Eq. (12), where E is the potential difference, k is Boltzmann's constant, T is the temperature, e is the electron charge, P₁ or P₂ is the pressure of the gas that is carried across the material at either one of the electrodes.

\[
E = \frac{kT}{4e} \ln \frac{P_1}{P_2}
\]  

This mechanism is often used in oxygen sensors, which are especially sensitive to oxygen since the defects in the lattice most often are oxygen vacancies and oxygen ions are able to diffuse through these vacancies. These sensors are called potentiometric. The binary lambda sensor, made of yttria-stabilized ZrO₂, is an example of a potentiometric metal oxide sensor. [8]

If a voltage is applied across the two sides of the material, the ion transport may be forced to go in a particular direction. Sensors based
upon this principle are called amperometric. The linear lambda sensor is an example of an amperometric metal oxide sensor. [8]

By adding grains of another material to the metal oxide, which is called doping, certain properties will be obtained. These properties may be increased selectivity to a certain species, increased speed of response and increased stability. The added material may also increase the catalytic activity and thereby make the chemical reactions on the sensor surface reach equilibrium faster. The doping material can be yttria such as in the case with zirconia. [7, 8]

The yttria-stabilized zirconia sensor is the most common lambda sensor in automotive applications today. There are several types of zirconia sensors, but they can be divided into two major groups; the linear and the binary sensors. Both types are based on the galvanic cell with yttria-stabilized zirconia, surrounded by two platinum electrodes.

![Diagram of Zirconia Sensor](image)

Fig. 6. (a) The ion current through the ZrO$_2$ electrochemical cell induces a potential difference. (b) The linear lambda sensor consists of two electrochemical cells.

The ZrO$_2$ sensor was first used in 1977, and has been modified several times since then. The detection principle of the zirconia sensor is based
5. Gasoline engines: Measuring the lambda value

on the dissociation of oxygen molecules on the pair of platinum electrodes and diffusion of oxygen ions through the zirconia. Provided that the concentrations of oxygen on the two electrodes are not equal, this gives rise to an oxygen ion gradient, which can be measured as either a potential across the electrodes or an ion current between the electrode pairs. The sensor is normally heated to a temperature of 650-750ºC, which makes it an ion conductor.

5.1.2. The binary zirconia sensor

The binary lambda sensor is potentiometric and consists of a piece of ZrO₂, attached to two Pt electrodes. One of the electrodes is in contact with the exhaust gases and the other electrode is placed in air. Oxygen molecules reach the Pt electrode, adsorb on the surface and dissociate. The oxygen atoms then diffuse through the ZrO₂ and form an ion current. The direction of the resulting ion flow is towards the lowest oxygen concentration, which in this case always is from the airside to the exhaust side electrode (Fig. 6.a). This ion current reaches equilibrium and creates a Nernst potential difference between the two electrodes. When the lambda value of the exhaust gases changes from a value above one to a value below one, there is a drastic change in the oxygen concentration at the exhaust side of the sensor. This makes the potential difference change from a very low value to a very high one; a binary switch. [10]

According to a specification for the Bosch lambda sensor the light-off time of the binary lambda sensor, that is the time before the sensor is ready to use, is less than 20 s. It has a heater power of 10 W and a service life of 160 000 km (a maximum of 10 years). Its operating temperature is 650-750ºC as mentioned above, but it can withstand temperatures of 930ºC, and at short moments even up to 1030ºC. At cold start, however, when there are droplets of condensed water running through the exhaust pipe, it is limited to a temperature of 350ºC. Zirconia is a material that is sensitive to thermo shock, and if it is heated to its operating temperature
when there is water in the system it may break. This means that the sensor is not ready to use until the water droplets in the engine are no longer formed.

The binary zirconia sensor is presently used by most car manufacturer for measuring the lambda value both before and after the catalytic converter. The lambda sensor before the converter is involved in the lambda closed loop control, while the other one is used for detecting catalytic converter failure.

5.1.3. The linear zirconia sensor

The linear lambda sensor consists of two ZrO₂ electrochemical cells where one of the electrodes of each cell is placed inside of a cavity and the other electrode in contact with air or exhaust gases (Fig. 6.b). Molecules from the exhaust gases are allowed to reach inside of the cavity through a small aperture in the cell on the exhaust-side of the sensor. A voltage is applied across the semi-conducting material of the cell that is in contact with air so that oxygen ions are pumped out of or into the volume. The difference in the oxygen concentration between the exhaust gases and the inside of the volume is kept constant by using the pumping zirconia cell for regulation. If the pumping voltage is chosen so that the voltage difference measured by the cell that is in contact with the exhaust gases is always kept at a constant level, the ion pumping current becomes a measure of the oxygen concentration in the exhausts. Since the sensor signal is the ion pumping current, this type of sensor is called amperometric. The linear dependence between the ion current and the lambda value can then be used for linear lambda measurements [11]. The major disadvantage with the linear zirconia sensor is that it is rather slow, due to the feedback loop used to control the current. [10]

The same technical data according to the specification for the Bosch lambda sensor is true for the linear lambda sensor as for the binary
5. Gasoline engines: Measuring the lambda value

Lambda sensor, when applicable. The sensor can measure lambda values between 0.7 and 2.0, and shows a sensitivity of 0.125 mA per percentage of oxygen. It is not truly linear, which means that data processing is required in order to use it as a linear lambda sensor.

5.1.4. The titanium oxide sensor

The titanium oxide sensor is a metal oxide sensor where the conductivity of the sensor material is taken as the sensor signal.

A titanium oxide sensor is commercially available at NGK Spark Plug Company in Japan [12] and has been used as a lambda sensor by Nissan Motor Company. The titanium oxide sensor has been produced since 1982. The advantage of this sensor is that it is faster than the zirconia sensor [13].

The material of the TiO₂ sensor is porous, which is required for making the sensor fast. TiO₂ is a semiconductor with a bandgap of 3.2 eV, that is, it has a very high resistance at room temperature. At high temperatures, above 300ºC, some of the oxygen atoms become gaseous and oxygen vacancies are formed. The amount of oxygen atoms that become gaseous is dependent on the oxygen partial pressure outside the sensor surface. The oxygen vacancies contribute with electrons in the conduction band. The oxygen atom has shared two electrons with another atom in the lattice, and when the oxygen disappears the two electrons are no longer shared and a vacant site is left. These electrons are loosely bound to their lattice atoms and will easily reach the conduction band, which means that when oxygen vacancies are formed, the resistance decreases. The resistance is strongly dependant on the temperature. The time to reach equilibrium is considerably lowered when the material is impregnated with a metal such as Pt. The switch point in lambda for the sensor depends on the rate constants, and may differ from the stoichiometric value if the temperature is low. If the
5. Gasoline engines: Measuring the lambda value

5.1. Oxygen sensors

Temperature is high, the sensor becomes almost an ideal oxygen sensor. Pt gives additional reaction paths, and thereby accelerates the equilibrium process. [14]

SrTiO$_3$ is another useful material for this purpose. For temperatures above 400ºC oxygen molecules diffuse through the material and give rise to a potential that can be measured. This material has been used for cylinder-specific measurements. At 1000ºC the sensor is very fast, and a response time of less than 5 ms can be achieved. By doping the material it is possible to modify the bulk concentration of oxygen defects and thereby change the response time. [9]

5.2. The field effect transistor sensor

5.2.1. Sensor principle

The field effect transistor (FET) sensor is based on a traditional metal oxide semiconductor transistor device, which is commonly used in electronic equipment (Fig. 7). The sensor device has however a catalytic material, a metal oxide or a conducting polymer as the gate material, which makes it sensitive to a wide range of species. By modifying the gate area in different ways it is possible to use the device in liquid applications, but the type of sensor that will be treated here is used for detecting gaseous species. Only the case where the gate material is a catalytic metal will be discussed. [15]

The sensor principle is based upon the change in the electric properties of the device that is induced by the presence of different gases. The gas molecules that adsorb on the catalytic surface will dissociate and diffuse to the metal insulator interface, where they will form a polarized layer, most likely on the insulator surface (Fig. 8). This layer changes the electric field within the insulator and thus affects the number of mobile carriers in the semiconductor. Since the current, which runs through the
device, is dependent on the number of carriers in the semiconductor, this will change the electronic properties of the component. [15]

![The structure of the MOSFET sensor.](image)

For simplicity, the gate and source of the sensor are often connected, which makes it a two-terminal device, whose properties resemble a diode. The behaviour of the device is often presented in an I-V (current-voltage) curve. When the polarized layer is formed at the metal-insulator interface, this will cause a shift in the I-V curve (Fig. 9). The sensor may be operated either in a constant voltage or a constant current mode, and gaseous species will thus be detected as a change in the current or in the voltage, respectively. The latter is the most common operation mode since it gives the highest reproducibility. [15]

The most extensively studied reaction that is involved in the gas sensitive properties of the MOSFET sensor device is that of hydrogen. The detection of hydrogen with a Pd gate MOSFET device was first discovered by Lundström et al in 1975 [16], and since then a lot of research has been devoted to model the details in the detection principle in the presence of this gas. It is clear that when the hydrogen molecules reach the catalytic material, they will dissociate and either combine with oxygen molecules from the ambient air that have also dissociated on the
surface, or diffuse through the catalytic material. The formation of hydrogen molecules is rare and can be neglected in the presence of oxygen. If the equilibrium concentration of hydrogen at the metal-insulator interface is calculated, this may be used for finding the expression in Eq. (13) [17], which relates the voltage shift to the hydrogen and oxygen pressures at the surface, where \( c_1 \) and \( c_2 \) are rate constants for the hydrogen adsorption and the water formation, \( \Delta V_{\text{max}} \) is the maximum voltage shift, and \( P_{H_2} \) and \( P_{O_2} \) are the pressures of hydrogen and oxygen, respectively. For Pd devices at a temperature higher than 100ºC, \( \alpha = 1 \). [15]

\[
\Delta V = \Delta V_{\text{max}} \frac{\sqrt{c_1 P_{H_2} / c_2 P_{O_2}}}{1 + \sqrt{c_1 P_{H_2} / c_2 P_{O_2}}} \tag{13}
\]

Eq. (13) is only valid for hydrogen since the detection principle for other molecules is not the same. The detection of other molecules may be divided into some different cases. In the case when the molecule contains hydrogen atoms to some extent, these molecules may reach the surface of the catalytic material and dissociate so that hydrogen atoms are again allowed to diffuse freely to the metal-insulator interface. In the case with molecules that do not contain hydrogen like CO and NO, however, the detection principle is different, since no other molecules than hydrogen are able to diffuse through the catalytic metal. This is also true for ammonia, although it contains hydrogen atoms. The catalytic film for detecting these molecules should be porous, so that the oxide is directly exposed to the gas. This makes it possible for dipoles such as CO and NO to form a dipole layer at the metal-insulator interface without diffusion through the metal. In the case with ammonia, it is believed that the triple points, where the gas, the insulator and the catalytic metal meet, are the key to the sensitivity. The ammonia molecule may here dissociate and react with oxygen so that some free hydrogen atoms are formed. The voltage shift for molecules other than hydrogen most often follows Eq. (14), where \( \beta \) depends on the reaction.
5. Gasoline engines: Measuring the lambda value

paths and P is the pressure of the reactants. $\Delta V_{\text{max}}$ is the maximum voltage difference and depends on the total amount of available sites and the dipole moment of the adsorbed molecules. Eq. (14) shows a Langmuir relationship, which for low pressures show a linear dependence of $P^\beta$ and for high pressures saturates at $\Delta V_{\text{max}}$.

![Diagram showing gas molecules reaching the catalytic gate metal](image)

Fig. 8. When gas molecules reach the catalytic gate metal, they dissociate, diffuse through the material and form a polarized layer at the metal-insulator surface.

$$\Delta V = \Delta V_{\text{max}} \frac{P^\beta}{1 + P^\beta}$$

(14)

For the field effect sensor Eq. (15) is valid, where $p_i$ is the dipole moment of adsorption complex i, $N_i$ is the number of available sites for that complex and $\varepsilon_0$ is the dielectric constant for vacuum [15]. Different complexes may occupy the same type of site. Knowledge about activation energies and adsorption/desorption energies will, however, make it possible to decide equilibrium conditions. The voltage shift, $\Delta V_{\text{max}}$, is often of the order of 0.5 - 1 V.

$$\Delta V_{\text{max}} = \sum_{i=1}^{n} \frac{p_i}{\varepsilon_0 N_i}$$

(15)
The selectivity of the MOSFET sensor very much depends on the type of catalytic gate material used, but also on the structure of the material and the temperature. However, the MOSFET sensor based on silicon fails electrically at temperatures above 250°C. In order to increase the usable temperature range for the device, the wide-bandgap semiconductor SiC has been chosen as the substrate. The devices based on SiC are called MISiCFET (Metal Insulator Silicon Carbide Field Effect Transistor) or simply SiC-FET sensors. These sensors may be operated up to 700°C, and have been working for short periods up to 1000°C [18]. At temperatures above 500°C the reactions taking place on or at the catalytic material are very fast, and the gas response may have a time constant of a few milliseconds. [19, paper II]

![Fig. 9. The polarized layer affects the electrical characteristics of the device.](image)
5. Gasoline engines: Measuring the lambda value

5.2.2. The SiC-FET lambda sensor

The SiC-FET lambda sensor has been shown to be suitable for use as a selective linear lambda sensor [20]. When working as a lambda sensor, the SiC-FET sensor responds to changes in the gases that are mentioned in Eq. (2). Since it is based on SiC, it withstands harsh environments such as in the car engine, and due to the properties of SiC it is believed to be more thermo shock resistant than the yttria-stabilized zirconia lambda sensor. Another advantage is that it is faster than the traditional lambda sensor so that it detects changes in lambda more quickly.

The SiC-FET sensor is based on the MOSFET principle, but its design is somewhat special. The conductive channel between source and drain is buried deeper down in the semiconductor, in order to protect it from surface states at the semiconductor-insulator interface and the harsh environment (Fig. 10). The device has been designed and processed by ACREO in Kista, Sweden. The source and gate are short-circuited and connected to ground, while a positive potential is applied to the drain. The SiC-FET sensor is also a short-channel device, which means that the conductivity of the channel does not only depend on the gate potential,
but also on the potential difference between the drain and the source. Moreover, these properties of the SiC-FET sensor open up possibilities to e.g. change the baseline of the device through an externally applied voltage on the substrate. The SiC-FET sensor is normally operated at a constant current of 100 µA, and the change in voltage between source and drain is taken as the sensor signal. [15]

The SiC field effect sensor has been tested for air-to-fuel ratio sensing since 1997 [21], but then the transducer was a SiC capacitor instead of a transistor. SiC capacitors are further described in section 7.3. The MISiC lambda sensors were first used as transistor devices at the end of the 90s. In a publication by Tobias et al the function of this device during lambda sensing was demonstrated [22]. The MISiCFET sensors have also proven to be fast enough for detecting if one cylinder has a deviating lambda value, i.e. cylinder-specific measurements [20]. In this thesis the ability of the SiC-based field effect sensor to detect lambda has been further tested. For example, engine measurements have been done together with selectivity tests. These experiments are described in Paper I.
As was mentioned in the introduction, one way of reducing the amount of nitrogen oxides from diesel driven cars is to add urea to the exhausts. This method is called SCR (selective catalytic reduction). The urea will decompose into ammonia at the high temperature (Eq. (16)) [23] and will react in a special catalytic converter with the nitrogen oxides to form nitrogen and water according to Eq. (17), where x is either 1 or 2.

\[
(NH_2)_2CO + H_2O \rightarrow 2NH_3 + CO_2 \] \tag{16}

\[
(12/x)NO_x + 8NH_3 \rightarrow (6/x + 4)N_2 + 12H_2O \] \tag{17}

This is, however, not the only method under development for reducing nitrogen oxides from diesel engines. One alternative is to use a material with a high storage capacity for nitrogen oxides, which will work as a trap for the gas [24]. When the trap has stored a significant amount of nitrogen oxides the composition of the air to fuel mixture is manipulated so that the lambda value is below one for a short while. This pulse of exhausts where the reducing gases are in excess removes the oxygen from the nitrogen oxides. Another method is to add hydrocarbons instead of urea to the exhausts after combustion, and let the nitrogen oxides react with the hydrocarbons in the catalytic converter, so-called HC-SCR [25]. A third alternative that deserves attention is the EGR (exhaust gas recirculation) method where the oxygen contents of the fuel mixture and the flame temperature are decreased by adding exhaust gases to the injection chamber [26]. All these methods have the ability to reduce the amounts of nitrogen oxides in the exhausts from diesel driven vehicles. However, the major benefit with using ammonia SCR for reducing nitrogen oxides is that the efficiency of the conversion is very high; Daimler Chrysler has reported that up to 90% of the nitrogen oxides can be reduced to harmless species [27]. This efficiency was reached
provided that an oxidation catalyst was used, for oxidizing NO to NO₂, together with the SCR catalyst and by utilizing closed loop control. The other methods give a significantly lower efficiency.

The disadvantage with ammonia SCR as compared with the other methods, however, is the difficulty to distribute urea to customers in a convenient way. All other methods can be used with existing tanks and tank stations, while ammonia SCR requires both an extra tank for urea and special filling station equipment. Moreover, the major challenge with the SCR system in itself is how to add a proper amount of urea to the exhaust gases. This may be dealt with through building a model for the amount of urea that should be added based on the driving conditions and measured engine parameters. Such a model, however, may be difficult to achieve, and the amount of nitrogen oxides that are let out in the environment will most likely exceed the legislated levels. A much more well-controlled way of regulating the system is to use sensors that are sensitive to either ammonia or nitrogen oxides or both. This system will make use of closed loop control in a similar way as for regulating the lambda value in a gasoline engine. The responses from the sensors will give information to the urea injector on whether there is ammonia or nitrogen oxides in excess in the exhausts, and the injection of urea will be adjusted according to these signals. The ammonia sensor may also be used for OBD (on board diagnosis), where detection of ammonia after the catalytic converter indicates that the converter does not function properly.

One of the scopes of this thesis is the development of an ammonia sensor for measuring ammonia slip from an SCR system. The sensor primarily presented in this thesis is based on the SiC-FET technology, as described in section 5.2.2, and it is one of the sensor technologies currently tested for SCR systems at Ford Research Laboratories (Dearborn, Detroit, USA) and Volvo Technology (Gothenburg, Sweden). However, there are also some other sensor technologies that
have been shown to successfully detect ammonia. These competing technologies are the zeolite-based sensor, the mixed potential sensor and the molybdenum oxide sensor, which are presented in the following chapters. In chapter 6.4 a short summary of the previous research on the SiC-FET device as an ammonia sensor is given.

6.1. The zeolite-based sensor

Zeolites are alumosilicates, that have a specific atomic relation between the amount of silica and alumina (SiO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3}). Aluminum that replaces silicon in the lattice has to be charge compensated due to the different valences of the two ions. The ions that are used for charge compensation may be small species such as protons or ammonium ions. These ions are mobile in the lattice and give rise to ionic conductivity. The only species present in diesel exhaust gases that may act as charge compensators are hydrogen and ammonia. This means that in the absence of ammonia protons will occupy the sites in the zeolite and the conductivity will be determined by the mobility of these when they move from site to site. In the presence of ammonia, however, the ionic conductivity is enhanced. This is most likely due to a decrease of the electrostatic attraction between the protons and the lattice, presumably because ammonium ions are formed. The ammonium ions will work as carriers for the protons and enhance their mobility. Thus, the presence of ammonia is detected as an increase in the conductivity of the zeolite film. The zeolite-based sensor has been shown to be sensitive to low concentrations of ammonia [27]. The influence of other species present in the diesel exhausts on the sensor signal is non-significant since only water and ammonia are expected to enhance the mobility of hydrogen ions and the concentration of water can easily be measured and compensated for. The temperature of operation for these devices is 480ºC, but they are stable up to a temperature of 800ºC, which makes them suitable for use in diesel exhaust gas.
6. Diesel engines: Measuring ammonia slip

6.2. The mixed-potential zirconia sensor

The mixed-potential zirconia sensor makes use of an yttria-stabilized zirconia cell, similar to the one used in the traditional lambda sensor, but one of the Pt electrodes has been covered with a second material. This material may be chosen to fit the application, but if a NO\textsubscript{x} sensor is desired a mixed-metal oxide such as CdCr\textsubscript{2}O\textsubscript{4} has been shown to be among the most suitable. When nitrogen dioxide detection is desired the term mixed-potential refers to the potential that is required for the two reactions described in Eq. (18) and (19) to occur at a similar rate [28]. This sensing technology may be used for detecting ammonia simply by choosing another type of sensitive material.

\[ NO_2 + 2e^- \rightarrow NO + O^{2-} \]  \hspace{1cm} (18)

\[ 2O^{2-} \rightarrow O_2 + 4e^- \]  \hspace{1cm} (19)

The benefit with this type of sensor technology is that the methods behind processing yttria-stabilized zirconia are well-developed and that the material has proven to withstand the harsh environment of the engine exhausts.

6.3. The molybdenum oxide sensor

The molybdenum oxide sensor is a metal oxide sensor based on the n-type semiconductor molybdenum trioxide. The change in electrical conductivity when the sensor is exposed to different gases is taken as the sensor signal. Further information on the sensing principle of metal oxide sensors can be found in section 5.1.
6. Diesel engines: Measuring ammonia slip

The molybdenum oxide sensor has been shown to be sensitive to gases such as ammonia, hydrogen and nitrogen oxide [29]. At a temperature between 400 and 450ºC there is a peak in the ammonia sensitivity, and at this point the nitrogen oxide sensitivity is less than half of that for ammonia. The sensor responds linearly to an increase in the ammonia concentration at least up to 500 ppm and reacts to concentrations of less than 25 ppm.

6.4. The SiC-FET sensor

The SiC field effect sensor was first tested for the SCR project in 1999 [30]. The transducer was in that case a Schottky diode, and its selectivity for ammonia in synthetic diesel exhausts was shown to be good. The transistor device, of a slightly different design than in Fig. 10, was in 2000 shown to be able to detect ammonia added to diesel exhausts [31]. In this thesis engine measurements with the SiC-FET sensor is described, as well as the cross-sensitivity to NO₂ and the influence of water vapor. Further information on these experiments can be found in Paper IV.
7. The SiC field effect device

The SiC-FET sensor can be used as a sensor for both lambda and ammonia SCR closed loop control. The major difference between SiC-based devices and field effect sensors with Si as the substrate material is the possibility to use a higher operating temperature. Increasing the temperature creates an opportunity for detecting species that are non-reactive at low temperatures, such as hydrocarbons.

The ability of SiC-based sensors to work at high temperatures is due to the wide bandgap of the material, which allows operation without electrical breakdown. The sensor functioning is, however, not depending on the type of semiconductor used, which means that other wide bandgap materials such as GaN or diamond may very well replace SiC. Field effect components based on these materials have been reported to work satisfactorily as exhaust gas sensors. Schalwig et al [32] showed that GaN sensors are sensitive to e.g. hydrogen, carbon monoxide and nitrogen oxides that are normally present in exhaust gases, and Gurbutz et al [33] have demonstrated diamond FET devices working at 500ºC. The SiC-based field effect sensors are, however, the most mature in terms of material quality and available processing methods.

7.1. The properties of SiC

Silicon carbide is a material with many interesting properties. Due to its high band gap of 3.27 eV, as compared with Si that has a band gap of 1.12 eV, it can be used at high temperatures without becoming intrinsic. It is also chemically inert, and has a very high thermal conductivity.

Many different polytypes are energetically favored in the case with silicon carbide. It is possible to find stacking sequences in the material ranging from pure hexagonal to pure cubic, and over 200 polytypes have been
7. The SiC field effect device

found. Two of the most common polytypes are called 4H and 6H, where H stands for hexagonal and the number for how many atomic layers that are repeated in the stacking sequence. The 4H polytype has been used for constructing SiC field effect devices. This polytype has a slightly larger band gap than 6H-SiC.

These properties make silicon carbide a suitable material for use in exhaust gas applications. The atmosphere inside the exhaust pipe of an engine is very warm (up to 1000 degrees) and contains many different gases and particles, which create a very harsh environment. It is necessary to use a material that is chemically inert so that it does not degrade in this atmosphere. Also, the water droplets that are formed at cold start present a problem to overcome for the material, and SiC is believed to withstand this due to its hardness.

Silicon carbide components can, as well as silicon devices, be integrated with other circuits. Silicon carbide has not yet been so extensively studied as silicon, and the wafer size is still smaller. There are also still defects in the wafers that may cause problems in manufacturing devices, but this is most pronounced in applications such as power devices. However, new suppliers of silicon carbide have appeared on the market, and the wafer price is expected to decrease. Extensive research is performed on the development of high-quality devices, since such components are very attractive for applications in strong electric fields and at high frequencies. [34]

7.2. The different types of field effect sensors

The field effect sensor has been under development at Linköping University, Sweden, for more than twenty-five years. Lundström et al [16] discovered that an ordinary MOSFET with a Pd gate was sensitive to hydrogen gas, which made it highly suitable for use as a hydrogen sensor.
In order to be able to study the sensing principle further more easily, a capacitor was constructed, which was made up of only three parts; the semiconductor, an insulator and a catalytic metal (Fig. 11). Since then, many different catalytic metals and types of insulators have been investigated. At the beginning of the 90s the first attempts were made to use a field effect device based on SiC instead of Si [35-37]. As a way of separating these devices from the Si-based sensors, they were given the name "MISiC" (Metal Insulator Silicon Carbide). The new material made the sensor less sensitive to harsh environments, which opened up the possibility to use it for several new application areas. The SiC based sensor was at Linköping University first studied as a capacitor, due to its simple structure. However, since the electronics required for performing measurements on capacitors is rather complicated, there was a need for another structure. The Schottky diode device was developed for this purpose [30]. This structure has other disadvantages, though. Since it is necessary to run a current through the entire device, across the insulator, it degrades more easily, and the long-term stability is often poor. As a solution, the SiC based MOSFET device was developed [38], which had a combination of the advantages of both the capacitor and the Schottky diode. The structure of this sensor has been optimised and is designed and processed at ACREO in Kista, Sweden.

The three different types of field effect devices respond to changes in the gas ambient in a similar way; a polarized layer at the metal-insulator interface changes the electrical characteristics of the component. The theory behind the SiC-FET sensor was described in section 5.2.2. Presently this is the most frequently used component in the cold start and SCR projects, and it could be regarded as the most important device for this work. However, the capacitor and the Schottky diode are also of importance to describe somewhat further here, since preliminary tests of new gate materials are often tested with these devices. These devices will most likely also be used in the research projects in the future, and are treated in the two following sections.
7.3. **The SiC capacitor**

The SiC field effect capacitor is made up of three different parts; a semiconductor, an insulator and a catalytic metal. The insulator is about 100 nm thick and the semiconductor is either n- or p-doped.

The semiconductor capacitor is different from ordinary capacitors in that it has minority and majority carriers that highly influence the behavior of the device. The semiconductor in itself contributes to the capacitance of the entire device, which means that the total capacitance is the semiconductor capacitance, $C_s$, in series with the oxide capacitance, $C_{ox}$. This can be described according to Eq. (20).

$$C_{tot} = \frac{C_{ox}C_s}{C_{ox} + C_s} \quad (20)$$

A capacitance measurement is normally made in the form of a C-V measurement. During such a measurement, a high-frequency voltage is applied to the device, and its capacitance is measured. The amplitude of the alternating voltage is normally about 100 mV. If a bias voltage is added to the high-frequency signal, and varied over time, it is possible to find the dependence of the capacitance on the bias voltage. A plot of this dependence is called a C-V plot (Fig. 12).

The shape of the C-V plot can be explained by studying the properties of the component and how it is affected by different bias voltages. If an n-doped semiconductor is used, high positive voltages on the metal will attract majority carriers in the semiconductor close to the insulator. This mode is called accumulation. These majority carriers easily move back and forth in the semiconductor, which means that they follow the alternating voltage closely. The capacitance of a capacitor is normally described according to Eq. (21), where $\varepsilon_r$ is the permittivity, $\varepsilon_0$ is the...
dielectric constant in vacuum, \( A \) is the area of the two electrodes and \( d \) is the distance between the electrodes.

\[
C = \varepsilon \varepsilon_0 \frac{A}{d}
\]  

(21)

Fig. 11. The MOS capacitor consists of a semiconductor, an insulator and a metal put into contact with each other.

At a high positive voltage, when majority carriers are easily transported through the semiconductor material, it is as if the distance between two imaginary electrodes in the semiconductor is close to zero. This means that the capacitance of the semiconductor in this case is very high. In
such cases, the total capacitance according to Eq. (20) becomes close to the capacitance of the oxide, which is not dependent on the applied voltage.

Fig. 12. A C-V measurement is a plot of the capacitance as a function of the bias voltage. The formation of a polarized layer at the metal-insulator interface causes a shift of the capacitance at a certain voltage.

When the applied voltage is decrease the number of majority carriers at the oxide-semiconductor interface will decrease as well. At a slightly negative voltage a depletion layer will be formed. In the depletion layer the concentration of majority carriers is lower than in the bulk. The layer with a lack of majority carriers contributes to the total capacitance in the same way as if the distance between the electrodes becomes larger; the capacitance decreases.

At even larger negative voltages the area close to the insulator becomes not only depleted of majority carriers, but the negative voltage will attract so many minority carriers that a state called inversion is reached, where the number of minority carriers becomes higher than the number of
majority carriers. In this state, the situation is almost the same as in the case of accumulation, although the minority carriers do not move as easily as the majority carriers did. This means that at a high frequency (in the range of MHz) the carriers will not follow the alternating voltage and the depletion layer below the insulator will remain. The size of the inversion layer is not affected by further decreasing the bias voltage. If an alternating voltage with a lower frequency is applied (~1 kHz), though, there is enough time for the minority carriers to move, and the capacitance will reach a high value again.

![Diagram of a SiC Schottky diode](image)

*Fig. 13. The structure of a SiC Schottky diode.*

The presence of a dipole layer at the metal-insulator interface adds additional charge to the applied voltage, which means that there will be a shift in the C-V curve. The sensor signal is normally taken as the shift in voltage at a constant capacitance. [39]

### 7.4. The SiC Schottky diode

The Schottky diode consists of a semiconductor and a metal (Fig. 13). When they get into contact with one another, electrons are transported from the semiconductor to the metal, creating band bending in the semiconductor. Hence there will be a potential barrier for the electrons in the metal when crossing the interface between the metal and the
7. The SiC field effect device

semiconductor. This is called a Schottky barrier. If a positive potential is applied on the metal it becomes easier for the electrons to cross the interface. On the other hand, if a negative potential is applied on the metal, the barrier for the electrons in the semiconductor will be increased and no current flow will occur. The current-voltage characteristics of this type of device are shown in Fig. 14. In the most recently produced Schottky diodes a thin layer of oxide is deposited between the metal and the semiconductor. This layer is thin enough for the current to go through it and the electrical behavior of the component is not affected, but its lifetime is considerably increased and the stability of the gas response is increased [40].

![Fig. 14. Current Voltage characteristics of a Schottky diode at 400°C with a porous Pt gate electrode](image)

The presence of a dipole layer at the metal-insulator interface makes the Schottky barrier either larger or smaller, which changes the voltage across the device. The change in voltage is taken as the sensor signal. [41]
8. The sensitive layer

8.1. The catalytic gate materials and their properties

The catalytic metals most frequently used as gate materials for the SiC field effect sensors are Pt and Ir. These metals are neighbors in the periodic table and belong to the transition metals. They both have a high melting point - 1772 and 2410ºC, respectively - which is one reason why they are chosen in the high-temperature projects described here. The two metals are in many ways similar with regard to catalytic properties. One difference, though, lies in the temperature dependence of Ir- and Pt-gate field effect sensors when detecting ammonia. The Pt sensor is most sensitive to ammonia at a temperature around 225ºC while the Ir sensor gives its optimal response close to 300ºC (Fig. 15). This is one reason why the Ir sensor is most often chosen for the SCR project, since the operating temperature of field effect ammonia sensors is 300ºC. The operation temperature is chosen as a compromise between a temperature that is high enough to prevent exhaust gas molecules from sticking to the metal surface and that optimizes the ammonia response. The catalytic activity of the gate material is not the only property of the material that influences the behavior of the sensor. The deposition method is crucial for the performance, which may make the sensitive layer either porous or dense. A porous layer is used for detecting ammonia, while a dense film is proper for the cold start sensor project. It would be possible to achieve a good ammonia sensor also by choosing a thin metal layer. A thin metal will, as a consequence of metal atoms forming islands during deposition on an insulator, have porous structure and thereby allow the ammonia molecules to get into contact with the insulator through openings in the metal. However, the thin metal layer needs to be deposited by evaporation, which gives a film that does not adhere very well to the substrate. Therefore, it is difficult to use the lift-off technology for patterning of the gate contact that is important for the
processing of transistor sensors. Because of this Ir is instead deposited by sputtering, which makes the metal stick better to the substrate. Sputtering gives a more dense film, though, and in order to create good ammonia sensors the sputtering process needs to be performed at an elevated pressure so that a porous material is formed. The Pt sensors used for the cold start sensor project should be thick and dense, and therefore sputtering is the proper method to use. In order to make the Pt adhere even better to the substrate and increase the long-term stability a layer of TaSi₅ is deposited in between the metal and the insulator. The two deposition methods used here, sputtering and evaporation, are described in the following sections.

Fig. 15. The response versus temperature for sensors with (a) Pt and (b) Ir as the gate material.
8. The sensitive layer

8.2. Sputter deposition

Sputtering is a method that may be used for depositing metals as well as insulators. During deposition a plasma of a gas, such as Ar, is formed between two electrodes; the substrate on which the deposited film is desired and a target from which atoms or molecules for the film are taken. The target electrode is negatively charged compared with the substrate. The sputtering takes place in a chamber that has first been evacuated and then filled with Ar to a pressure from a few up to a hundred mTorr. Positive ions from the Ar plasma are driven towards the target by the applied potential. The ions hit the target and target atoms are physically ejected. These atoms pass through the plasma and deposit on the substrate. When depositing a dense film of Pt the pressure in the chamber is typically less than one mTorr, while porous Pt or Ir deposition requires an elevated pressure. The pressure influences the sputtering process by lowering the kinetic energy of the atoms that have been ejected from the target through gas-phase collisions. A higher pressure results in a shorter mean free path of the atoms. Thus, at an elevated pressure the kinetic energy of the atoms is low, which makes them form a metal film where the atoms are not so densely packed. Deposition of an insulator requires an alternating potential to be applied. Typically this can be done by applying a voltage with a frequency of 13.56 MHz, which is called RF sputtering. A schematic drawing of both a DC and an RF sputter system is shown in Fig. 16.

Most commonly, sputtering is performed by utilizing a magnetron. In a magnetron there is a magnet behind the target that creates a magnetic field perpendicular to the target. This magnetic field enhances the yield of ions from the plasma that collide with the target. The benefits of using a magnetron are, e.g., that sputtering may take place at a lower pressure and increased deposition rate. [42]
8. The sensitive layer

8.3. Evaporation

Evaporation takes place, opposite to sputtering, in vacuum and is a rather simple process that does not make use of any plasma. The material that is about to be deposited on a substrate is located in a crucible or some other type of holder in which it is heated to its evaporation or sublimation temperature. Evaporated or sublimated atoms then deposit on the substrate. The deposition rate is determined by thermodynamics, such as the vapor pressure as a function of temperature. The kinetic energy of the atoms impinging on the substrate surface is not as high as during sputtering, which means that the film achieved by evaporation is not as dense. [42] A schematic drawing of an evaporation system is shown in Fig. 17.

Fig. 16. A schematic drawing of a DC (left) and RF (right) sputter system [42].
8. The sensitive layer

Fig. 17. A schematic drawing of an evaporation system.

8.4. Long-term stability

As was mentioned in previous sections a sensor that is to be used in an engine system is required to have a very long durability. This sets high demands on the sensor, both on the transducer and the sensitive material. The largest obstacle to be overcome is to increase the long-term stability of the catalytic material. The most fragile parts of the entire SiC field effect transistor sensor today are undoubtedly the gold wires that are used for connecting the pads of the device to the surrounding electronic circuits and the glue that fixes the sensor chip to the heater. However, the holder used here is only for research purposes, and these problems may easily be overcome by choosing packaging methods that are more proper for building prototypes.

When a Pt metal film is exposed to an alternately reducing and oxidizing atmosphere at a high temperature it quickly starts to restructure. This
phenomenon is known as thermal etching [43]. During thermal etching the metal structure changes so that the most energetically favourable state is achieved. This may be, for example, a state where a certain crystal plane type is dominating. The restructuring is severe, especially at high temperatures. Different ways of avoiding this restructuring are presently tested in our laboratory. Such methods include depositing another, more stable material, such as SiO₂, on top of the Pt. Pt may also be mixed with an insulator or another metal so that a more stable compound is formed.
9. Methods

9.1. Production and mounting

The SiC-based field effect devices used in this work have been of two different types; field effect transistors based on the SiC transistor technology (processed at ACREO AB, Kista, Sweden) with a catalytic metal as the gate material (processed at Linköping University, Sweden) or Schottky diodes (with gate metal processed at Laboratory of Sensors, CITEI-National Institute of Industrial Technology, San Martin, Argentine). The insulator of the transistor device is formed by first growing a thermal oxide of SiO$_2$ on the n-doped SiC and then a layer of low-pressure chemical vapor deposition (LPCVD) nitride, Si$_3$N$_4$. The nitride is subsequently densified, which also gives a top layer of SiO$_x$. The total thickness of the insulator is 80 nm. The gate metal of the SiC-FET lambda sensor is constituted by a sputter-deposited layer of 100 nm Pt underneath which a 10 nm TaSi$_x$ layer is deposited in order to make the Pt stick better to the insulator. The gate area width is 50 μm and the length is 690 μm. The Schottky diode consists of a 4H-SiC substrate with a 5 μm epilayer, processed by Okmetic, with a 1 nm layer of SiO$_2$ on top of which a 1 μm layer of porous Pt is deposited by screen printing. The SiC-FET ammonia sensor has either a porous Ir or porous Pt metal gate, at a thickness ranging from 25 to 60 nm. The ohmic contact on the backside of the sensor, as well as the source and drain ohmic contacts of the transistor, consists of alloyed Ni with 50 nm TaSi$_x$ and 400 nm Pt deposited on top for corrosion protection. The TaSi$_x$/Pt layer also forms bonding pads of the device.

The sensors are mounted either three by three, in the case with the transistors, or one or two at a time, in the case with the Schottky diodes. They are glued on a ceramic heater (Heraeus) together with a Pt-100
9. Methods

element and mounted on a 16-pin holder, Fig. 18. This package is suitable for use both in field tests and in the laboratory. The operation temperature of the devices is 500°C in the lambda sensor application and 300°C in the SCR application. The sensor is run at a constant current of 100 µA and the voltage across the component is taken as the sensor output signal.

![Sensor holder with a heater, Pt-100 element, and sensor chip.](image)

*Fig. 18. The sensor holder with a heater (rectangular), a Pt-100 element (to the right) and a sensor chip (black square).*

In laboratory measurements the sensor chip is connected to electric circuits for applying the constant current to the devices, heating the sensors to the operating temperature and measuring the sensor voltages. The gases are supplied from a gas mixing system where the desired concentration of e.g. hydrogen or ammonia can be achieved.

During engine measurements a tube mounting is used for the sensors in order to cool the gases before they hit the sensors. The cooling of the gases is necessary since the exhausts are at a temperature of 200-500°C in the exhaust pipe and the 16-pin holder cannot withstand this...
temperature. It is also important to be able to control the temperature of the sensors during operation.

![Fig. 19. During engine measurements a tube mounting is used for cooling the exhaust gases before they hit the sensor surface.](image)

The tube mounting consists of two tubes with different diameter, and the inner tube can be regulated in position so that it reaches to the middle of the exhaust pipe, see Fig. 19. This mounting will, due to the ejector effect, bring the exhausts to the sensor while cooling the gases to a temperature of 200-300°C.

![Fig. 20. During the excursion in Spain a new design of the tube mounting was used.](image)
In order to test the sensors in a real environment on a diesel truck equipped with an SCR system a more robust and heat resistant tube mounting was designed and produced, according to Fig. 20. To make sure that the new tube mounting would cool the gases efficiently, it was computer simulated by Ilja Belov at ACREO and Jönköping University [44]. This was an important step in the production process and gave information e.g. on how many cooling fins were required and how the device could be simplified. One significant change in this tube mounting design compared with the old one was the placement of the inner tube at a distance from the center of the outer tube, which had been noticed in the simulations to be advantageous for the flow across the sensors.

**9.2. Lambda sensor for closed loop control**

The Pt-gate SiC-FET sensor has been tested as a lambda sensor both in engine measurements and in the laboratory. The engine tests were primarily performed on a stationary gasoline engine, but the sensors have also been tested in a vehicle run in city traffic. All engine tests were done in cooperation with Volvo Technology in Gothenburg, Sweden. The cross-sensitivity to gases commonly found in gasoline exhausts gases was studied in the laboratory of Applied Physics at Volvo Cars, Gothenburg, Sweden, together with the linearity of the sensor in lambda stairs in the laboratory of S-SENCE, Linköping University, Linköping, Sweden. The lambda stairs were performed by varying the concentration of e.g. hydrogen, oxygen or carbon monoxide in order to get a specific lambda value. Speed of response tests were performed utilizing the MGO (moving gas outlet) system. The MGO equipment has been constructed by Tobias et al [43]. The sensor holder is mounted on a plate, which in turn is connected to a small electrical engine device. Under the plate are two gas outlets. When the electrical device is running, it moves the gas outlets under the sensor holder back and forth over the sensors at a
certain frequency (3-25 Hz), see Fig. 21. When two different gases are flowing in the two gas outlets and the electrical device is running, the gas ambient surrounding the sensors is changed rapidly. The sensor signal is then sampled with a frequency of 1 kHz, which makes it possible to determine the response time within ms. The experiments are further described in Paper I and II.

![Fig. 21. The speed of response was studied using the MGO equipment.](image)

During the measurements in a vehicle run in city traffic it was found that the sensors initially show a rather binary behavior, while they turn out to be more linear after being used for a longer while. This was further studied in the laboratory in Linköping, both by performing SEM studies and lambda stairs (Paper III). During these tests and the speed of response experiments the screen-printed Schottky diode was also used.

### 9.3. Ammonia sensor for SCR systems

The ammonia sensor has been tested in cross-sensitivity experiments in the laboratory at Volvo in Gothenburg, Sweden, at Ford Research Laboratories in Dearborn, Michigan, USA, and at Linköping University, Linköping, Sweden. Engine measurements at Volvo Powertrain,
9. Methods

Gothenburg, Sweden, have also been performed, both on stationary engines and in a running vehicle during an excursion to Sierra Nevada, Spain. These measurements are further described in Paper IV. Speed of response tests have been performed in the laboratory of S-SENCE and Applied Physics, Linköping University, Linköping, Sweden (Paper II)
10. Results

10.1. Lambda sensor for closed loop control

The lambda sensor has been shown to be selective to lambda among other gas compositions commonly present in gasoline exhaust gases. There is a small cross-sensitivity to carbon monoxide. The linearity studied in lambda stairs was found to depend on whether hydrogen, oxygen or carbon monoxide was varied to get a particular lambda value. This is interesting from a basic research point of view but the concentration ranges in these stairs were not the same as in a typical exhaust gas mixture. The speed of response was found to be below ten milliseconds (Fig. 22), which makes the device fast enough for being used for closed loop control. These results are further described in Paper I and II.

![Fig. 22. The time constant of SiC-FET lambda sensors is in the order of milliseconds.](image)

The connection between gate metal restructuring and the linear or binary response of lambda sensors was studied by comparing lambda stairs with
10. Results

SEM pictures. It was found that a highly discontinuous film gave a linear response, while a more dense film showed a binary behavior (Fig. 23). This is further discussed in Paper III.

![SEM pictures](image)

**Fig. 23.** (a) The gate metal (below) of a lambda sensor with binary behavior (above) was found to be denser than (b) the gate metal (below) of a lambda sensor with linear behavior (above).

10.2. Ammonia sensor for SCR systems

The ammonia sensor has been tested both in the laboratory and in engine measurements. Stationary engine measurements, performed together with Henrik Svenningstorp at Volvo Technology, have shown that the sensor is sensitive to ammonia in the exhausts (Fig. 24), even though other gas components may vary in a similar way, which makes it difficult to evaluate the data. However, previously pure ammonia has been injected in a diesel exhaust system and detected by the SiC-FET
sensors, which indicates that the sensors are in fact responding to ammonia in diesel exhausts. Testing the sensors during an excursion to Spain has this far shown that the sensor mounting is robust enough for this type of measurement. The weakest parts of the device are in fact the glue and the bonding wires. The cross-sensitivity to NO₂ as well as the influence of water vapor has been studied at Ford Research Laboratories by David Kubinski, and both these gases were found to affect the sensor response only to a small extent. The results are further described in Paper IV.

Fig. 24. The signals from the optical ammonia reference instrument and the two MISiC-FET sensors when detecting ammonia slip from an SCR system where the added urea has been computer controlled in a stair-like fashion.
11. Future work

The emphasis of the future work on the development of SiC-FET lambda sensors for cold start and SCR control will be on increasing the long-term stability of the devices as well as further experiments on the sensitivity and selectivity.

In the measurements performed this far it has been noticed that the lambda sensors show a step in their linearity when going from a lambda value under to above 1.06 (Fig. 23). The reason for this will be further studied. Also, in order to increase the knowledge on how the sensors respond to different species in the exhaust gases their sensitivity to N\textsubscript{2}O will be thoroughly investigated.

Increasing the long-term stability is of uttermost importance for the devices to work as exhaust gas sensors. Attempts to increase the long-term stability is in the scope of a diploma work presently performed on the SiC-based field effect sensors, and new materials as well as protecting layers will be extensively investigated in the future. The intention is to co-sputter the catalytic gate metal with an insulator or another metal and thereby prevent the material from restructuring.

It is also of large interest to study the transducer further, e.g. by letting transistor devices without gate metal be exposed to a particular gas environment and follow the long-term behavior. This will give information on the stability of other parts of the device than the gate, such as contact pads or the transistor doping.

Measurements will also be performed to increase the general knowledge about the component with a buried channel. These experiments will partly be done during a shorter stay as a guest researcher at Ishinomaki University, Japan, in summer 2004.
A cooperative project together with the Department of Electrical Engineering is planned for autumn 2003. In this project the SiC-FET sensor will be tested for cylinder-specific monitoring and control of the lambda value.

Moreover, measurements on GaN-based devices from Walter Schottky Institut in Munich, Germany, have been performed previously (Paper V). This cooperative effort will continue and will give further insight in the development of sensors based on wide bandgap materials other than SiC.

The primary goal of this work is to bring the sensors closer to being commercially available for the applications treated in this thesis. The precise nature of the future research with that goal in mind cannot yet be given in detail, and the experiments mentioned above are just a few examples of the work that will follow.
12. References


12. References


12. References

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