New Materials for Gas Sensitive Field-Effect Device Studies

Anette Salomonsson
Gas sensor control is potentially one of the most important techniques of tomorrow for the environment. All over the world cars are preferred for transportation, and accordingly the number of cars increases, unfortunately, together with pollutants. Boilers and powerplants are other sources of pollutants to the environment. Metal-Insulator-Silicon Carbide (MISiC) Field-effect sensors in car applications and boilers have the potential to reduce the amount of pollutants. These devices are sensitive to several gases in exhaust and flues gases, such as hydrogen, hydrocarbons, and ammonia (for the selective catalytic reduction (SCR) application). These applications require specific and long term stable sensors. The car industry for instance wants sensors that will stand at least 240 000 km.

This thesis presents studies of the active layers in MIS Field-effect gas sensors. Fundamental studies of the sensor mechanism has been performed in ultra high vacuum, UHV, to understand the gas response mechanism in more detail, and to find out how the sensing mechanism is affected by the catalytic active gate material. The influence of four different insulating layers was studied at atmospheric pressure. The catalytic layer has also been altered to metal oxide nanoparticles with or without impregnation of catalytic metals.

Nanoparticles are potential candidates to be used as the gate material for high temperature, long-term stable FET sensor devices. The combination of catalytic metals and metal oxides may prevent reconstruction of the metal. The use of nanoparticles will increase the number of triple points (catalytic material and insulator in contact with gas), which are crucial e.g. for the ammonia sensitivity. Another challenging aspect of nanoparticles is the possibility to get selectivity to different gases based on the particle size.
The goal is to find new sensitive, selective and more long term stable materials, which meet the requirements above.

From the UHV studies we learned that the two catalytic active metals Pt and Pd, do behave in a similar way, although there are some quantitative differences. Values for the heat of adsorption on both the Pd and Pt surfaces are estimated as well as the dipole moments for the adsorbates on the insulator surface.

The insulators play an important role in the sensing mechanism, since the adsorption of hydrogen atoms (or protons) that are detected by the sensor occur on the insulator surface. By changing the insulator material the saturation response of the sensors is affected. It was shown that Al₂O₃ gave a higher saturated response to hydrogen in Pt-MIS capacitors at 140°C as compared to Ta₂O₅, SiO₂, and Si₃N₄.

We have tested wet synthesized ruthenium dioxide and ruthenium nanoparticles, which are electrically conducting and catalytically active sensing material. RuO₂ is especially interesting as a high temperature material since it is already oxidized. Both materials show a sensitivity pattern comparable to porous platinum. The temperature dependence of the gas response indicates a higher catalytic activity of the RuO₂ as compared to Ru nanoparticles.

Nanoparticles synthesized by aerosol technology provide several advantages like a good adhesion of the particles to the substrate, many possible material combinations and efficient methods for particle separation according to size. The methods to use this technology for sensing materials in MISiC sensors are now under development and some preliminary results are obtained.
Till Per, Adam och Axel
I. Hydrogen Interaction with Platinum and Palladium Metal Insulator Semiconductor devices
   Anette Salomonsson, Mats Eriksson, Helen Dannetun
   Journal of Applied Physics, accepted for publication

II. The influence of the insulator surface properties on the hydrogen response of field-effect gas sensors
    Mats Eriksson, Anette Salomonsson, Ingemar Lundström, Danick Briand, A. Elisabeth Åbom
    Journal of Applied Physics, accepted for publication

III. Nanoparticles for long-term stable, more selective MISiCFET gas sensors
    Anette Salomonsson, Somenath Roy, Christian Aulin, Judith Cerdà, Per-Olov Käll, Lars Ojamäe, Michael Strand, Mehri Sanati, Anita Lloyd Spetz
    Sensors and Actuators B, 107(2), pp 831-838, 2005

IV. RuO$_2$ & Ru Nanoparticles for MISiCFET gas sensors
    Anette Salomonsson, Somenath Roy, Christian Aulin, Lars Ojamäe, Per-Olov Käll, Michael Strand, Mehri Sanati, Anita Lloyd Spetz

V. Nanocrystalline Ruthenium oxide and Ruthenium in sensing applications - an experimental and theoretical study
   Anette Salomonsson, Rodrigo M. Petoral Jr., Kajsa Uvdal, Christian Aulin, Per-Olov Käll, Lars Ojamäe, Michael Strand, Mehri Sanati, Anita Lloyd Spetz,
   Journal of Nanoparticle Research, submitted

VI. Aerosol deposited particles as gate material for MISiC-capacitor sensors
    Anette Salomonsson, Michael Strand, Doina Lutic, Per-Olov Käll, Lars Ojamäe, Mehri Sanati, Anita Lloyd Spetz, manuscript
CONTRIBUTIONS TO INCLUDED PAPERS

Paper I
I planned the experiments together with Prof. Helen Dannetun and Docent Mats Eriksson, and did all of the experiments, apart from the AFM analysis and the second order experiments which were performed by Dr. Elisabeth Åbom and Eriksson. I made most of the modeling except those about “second order adsorption”. These studies were made by Eriksson. I took part in the writing.

Paper II
Experiments made by Docent Mats Eriksson, Dr. Lisa Åbom and me. Auger analysis was made by Eriksson. The new insulators were produced by Dr. Danick Briand. I took part in the writing.

Paper III
I was the project leader. I planned the experiments, produced all samples except from the synthesis of the particles, which were made by the diploma worker Christian Aulin. He also made the XRD analysis of the produced powders. The sensor measurements were made by me and Dr. Somenath Roy, and the evaluation was made by me. I wrote the first manuscript and was together with Somenath responsible of writing the final paper.

Paper IV
I was the project leader. The synthesis and the evaluation of the particles were made as in Paper III. I made all the experiments and all the evaluation. I was responsible for writing the major part of the paper.

Paper V
I was the project leader. I planned all the experiments and preformed all the sensor measurements. The XPS studies were made by Rodrigo M. Petoral Jr. and the computational calculations were made by Docent. Lars Ojamäe. I wrote the paper, except for the parts that Petoral and Ojamäe were responsible for.

Paper VI
I was the project leader. The aerosol deposition of nanoparticles were made by Dr. Michael Strand and Dr. Doina Lutic. I planned and supervised the gas measurements made by Doina. The evaluations of the measurements were made by me together with Doina. The SEM pictures were made by Helena Wingbrant. I wrote the manuscript except for the experimental part of aerosol synthesis, which is written by Strand.
VIII. Metal oxide Nanoparticles as Novel Gate Materials for field-Effect Gas Sensors
S. Roy, A. Salomonsson, A. Lloyd Spetz, C. Aulin, P Käll, L. Ojamäe, M. Strand, M. Sanati
*International Symposium on Advanced Materials and Processing, (ISAMAP2 K4) Kharagpur, India, 6-8 December, 2004*

IX. Pt/γ-Al2O3 particles for long term stable, highly selective MISiCFET gas sensors
Judith Cerdà, Anette Salomonsson, Michael Strand, Mehri Sanati, Anita Lloyd Spetz
*The 10th International Meeting on Chemical Sensors, (IMCS 10), Tsukuba, Japan, July 11-14, 2004*

X. HDO formation studied on hydrogen sensitive Pd- and Pt-MIS devices
A. Salomonsson, Mats Eriksson, Helen Dannetun
*22nd European Conference on Surface Science, (ECOSS 22), Praha, Czech Republic, September 7-12, 2002*

XI. Surface and Interface adsorption of Hydrogen on Pt-SiO2-Si Structures
A. Salomonsson, M. Eriksson, L.-G. Ekedahl, H. Dannetun
*20th European Conference on Surface Science, (ECOSS 20), Krakow, Poland, September 4-7, 2000*

XII. Purity and surface structure of thick 6H and 4H SiC layers grown by sublimation epitaxy
Mikael Syväjärvi, R. Yakimova, E. A. M. Johansson, A. Henry, Q. Wahab, C. Hallin, E. Janzén,
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INTRODUCTION

1.1. General

The environment is of great concern to everyone. We have to deal with pollutions and global warming that maybe will change the climate drastically in the near future. Vehicles contribute a great deal to the pollutants. There is development concerning alternative fuels, but so far these have to be considered as future fuels, since more research is needed before they are applicable to our community. For instance the infra structure has to be adapted for using $H_2$ as fuel. Already there are vehicles using alternative fuels such as ethanol and bio-fuels, although the access of fuel is limited. The vehicles of today in the mean time need to be improved so that they become even more environmentally friendly. As an example combined fuels, like the ones mentioned above, together with gasoline or diesel should be possible to use in the same engine. Already there are experiments and tests with fuel-cell cars and buses which run on hydrogen [1]. However, also the vehicles of today (that will be here for a long time) needs further development.

Sensors that can regulate the combustion in an engine (or any combustion e.g. in boilers) to minimize the pollutants that are emerged is an important issue. Our research concerns sensors that are sensitive towards hydrogen containing gases. These sensors can be used to monitor the air/fuel-ratio, as the well known lambda-sensors, or as an ammonia sensitive sensor for control of selective catalytic reduction (SCR) [2].
The hydrogen sensitivity of catalytic metal-insulator-semiconductor (MIS) devices has been known for 30 years [3]. With Pd, Pt or Ir as the metal gate the electronic properties of the device are influenced by hydrogen and the device can thereby be used as a gas sensor for hydrogen and hydrogen containing gases. Hydrogen sensors will no doubt be of great interest in the future, when hydrogen is expected to play an increasing and important role in power production. Hydrogen detection will for example be essential during hydrogen production or for hydrogen storage purposes.

Field-effect devices based on silicon are limited to operation temperatures below approximately 200°C. The selectivity of field-effect devices for gas sensing is improved if the range of operation temperature is increased. One way to solve this problem is to change the semiconductor material into a semiconductor with a larger bandgap e.g. silicon carbide (SiC), (3.2 eV for the 4H polytype as compared to 1.1 eV for Si). The choice of the catalytic gate material will of course be critical for the sensitivity and selectivity of the devices.

The first part of the work presented in this thesis concerns a fundamental study of Pt-based MIS devices, where hydrogen adsorption on the Pt surface and at the Pt-insulator interface is in focus. The influence of the insulator surface properties of Pd/Pt MIS devices has been investigated. In the second part of the thesis nanoparticles have been used as a new gate material. By using metal oxide nanoparticles as the gate material of SiC-FET sensors the high surface area and the specific properties of small particles are benefited. A variety of sensing layers may be explored with the intention to enhance the selectivity. The gate material in SiC-FET devices needs to be conducting and this is most important for the capacitor devices. In the case of porous catalytic metals as gate material the metal tend to sinter at high operation temperature, which causes drift and reduced sensitivity [4]. Nanoparticle made of catalytic metals and support-materials may reduce the sintering effect.
2.1 **Gas sensors in general**

There are almost as many definitions of the word sensor as there are people. According to the Swedish dictionary, Nationalencyklopedin, 2005 [5]:

”En sensor är en anordning som känner av absolutvärdet eller ändringen av en fysikalisk storhet som tryck, temperatur, flödeshastighet eller pH-värde eller intensiteten för ljus, ljud eller radiowågor och omvandlar informationen till en form som lämpar sig för ett datainsamlande system.”

”A sensor is a set up that senses the absolute value or the change of a physical unit, such as pressure, temperature, flow or pH-value, or the intensity of light, sound or radio waves and transfers the information to a shape that is suitable for data collecting systems.”

From Wikipedia, 2005 [6] one can read:

“A sensor is a technological device or biological organ that detects, or senses a signal or physical condition and chemical compounds.”
Or simply, a chemical gas sensor converts a chemical state into an electrical signal [7].

There are almost as many types of gas sensors as there are ways that a gas can interact with sensor materials. The interaction can be in form of chemical reactions, adsorption, absorption etc. These interactions induce changes in e.g. resistivity, mass, work function, or in the reflection indices.

There are numerous types of gas sensors. One common type is the semiconducting metal oxide sensor (MOS). The sensing principle is based on resistivity changes in the metal oxide [8]. The most common, the SnO₂ sensor, is a sensor used for detecting reducing gases such as CO and combustible gases, e.g. C₃H₆. In pellistor sensors, the heat released during oxidation of a combustible gas on the (catalytic) sensor surface is the sensing signal [9]. Gas sensitive Metal-Insulator-Semiconductor Field-Effect Devices (MIS-FET) is the sensor device used in this work that detects charges or polarization of the gate.

2.2 The Metal Insulator Semiconductor structure

The MIS sensor structure has a catalytically active and hydrogen permeable material as gate contact. In the mid seventies Lundström et. al. [3, 10] discovered that MIS-FETs with a catalytic metal as the gate can be used as hydrogen sensors. Another breakthrough was made when it was discovered that a porous metal film makes the structure sensitive to gases such as NH₃, not detected with MIS-sensors with dense films [11, 12]. Nowadays a variety of devices using different materials and structures have been developed. Combining many sensors and applying pattern recognition methods makes it possible to improve the selectivity.

The sensing mechanism has thoroughly been studied mainly for Pd-MIS structures in ultra-high-vacuum (UHV) [13-15].
This thesis deals with improvement of our knowledge by studying platinum as the gate material, the role of the insulator and in the second section testing nanoparticles as the gate material. The aim is to develop sensors that are more selective, more suitable for high temperature environments and more long time stable. The studies performed in UHV (Paper I), has a two fold ambition: To use the device as a model system in catalysis and to reach a fundamental understanding of the sensing mechanisms of the Pt-MIS device. For the last purpose, also investigations at atmospheric pressure, were performed, studying the influence of the insulator surface on the sensor signal. To test new gate materials suitable for gas sensing the technology of using nanoparticles as gate material was developed.

2.3 The gas sensing principle

The hydrogen sensing mechanism of the Pt-MIS device is schematically presented in Figure 2.1.

Figure 2.1. Schematic picture of hydrogen sensing with a MIS-device. The different processes that take place are adsorption, dissociation on the outer surface, diffusion of hydrogen through the gate material and adsorption at the metal-insulator interface.
Hydrogen in the ambient interacts with the Pt surface where the hydrogen molecules adsorb dissociatively. Some atoms will diffuse through the metal film and adsorb at the Pt-insulator interface, while others desorb.

At the interface the hydrogen atoms form a polarized layer. This polarization causes a voltage shift, $\Delta V$, of the capacitance versus voltage curve, see section 2.5. The shift is the sensor output and is usually (typically) measured at a constant capacitance (the sensor signal), and is a function of the concentration of the interface adsorbates.

The detection of some gaseous species, such as ammonia, requires the use of a porous gate material. There are special sites (triple phase boundaries were the gate material, and the insulator are exposed to the gas phase on the gate region where ammonia, NH$_3$, molecules are dissociated and provide hydrogen atoms (or protons), which form the dipole layers at the interface.

Use of catalytic metal/metal oxide nano particles as the gate material has the potential to increase the occurrence of triple phase boundaries where the catalytic gate material, the insulator and the test gas molecules are in contact.

By altering the insulator and the surface properties of the insulator, parameters such as the sensitivity and the selectivity of the sensor are affected. It has been shown that the response is mainly due to trapping of atomic hydrogen or protons on the insulator side of the metal-insulator interface [17]. AFM studies by Åbom et al. revealed that, for devices with a high gas sensitivity, the metal surface facing the insulator has a hollow structure, see Figure 2.2 [18].

DRIFT (Diffuse Reflectance Infrared Fourier Transform Spectroscopy) studies, gave clear evidence that the hydrogen atom or proton form OH-groups on the silica surface for samples with Pt/Ir particles supported on silica [19].
Figure 2.2. Two examples of a close up of the metal -
insulator interface. The metal has been ripped off from the
oxide. Both the surface of the metal (that faced the
insulator) and the surface of the insulator are investigated
by AFM. a) 20 nm Pt sputtered at ambient temperature and
at 3 mTorr, and b) 20 nm Pt sputtered at ambient
temperature and at 60 mTorr. The rougher metal surface in
b) has shown to be advantageous for large hydrogen
sensitivity. (From Åbom et al in ref. [16].)

2.4 MIS capacitors

A MIS capacitor has three parts: the semiconductor, the
insulator and the metal (see Figure 2.3. and 2.4.). The
capacitors used in this work differ in semiconductor and
insulator material, as well as the active contact material.

For an ideal MIS-capacitor with n-type semiconductor
and a high positive voltage (+V) applied to the metal, the
majority carriers (electrons) gather at the semiconductor
insulator interface (accumulation) see Figure 2.3 (top, right).
The majority carriers are highly mobile and are easily
transported through the semiconductor material which acts as
a conductor.

When a small negative (-V) voltage is applied the
majority carriers (electrons) are repelled and the
semiconductor is depleted of mobile carriers, see Figure 2.3 (middle, right). This region is called the depletion layer. The negative charge on the metal is compensated by the static positive charges of the doping atoms in the depletion layer. Applying a negative voltage to the metal will cause the total capacitance to decrease, see section 2.5.

![Diagram showing charge distribution in p-type and n-type Si for different applied voltages](image)

**Figure 2.3.** The charge distribution in p-type Si, to the left, and to the right the charge distribution in n-type Si for different applied voltage on the metal.

As the applied voltage decreases even more the number of minority carriers (holes) at the surface finally becomes
larger than the number of majority carriers (electrons) and the surface is inverted, inversion is reached, see Figure 2.3 (bottom, right).

The corresponding charge distribution in a p-type device is shown in Figure 2.3 to the left. Metal Insulator Semiconductor Field Effect devices used as gas sensors can be of different kind, transistors, diodes or capacitors, see Figure 2.4. This work deals only with capacitors and therefore only these are described here.

![Figure 2.4. MIS-devices that are used as gas sensors.](image)

### 2.5 C(V) curves

In Figure 2.5 typical capacitance versus voltage (C(V)) curves using an n-doped semiconductor at low temperature (T<RT) and high frequency (f ≥ 1MHz) are shown. The shape of the C(V)-curves varies with the doping of the semiconductor material, measurement frequency, temperature etc. (see e.g. references [15, 20]).

Three parts of the curve are distinguishable: accumulation, depletion, and inversion, see section 2.4. The total capacitance is actually the semiconductor capacitance, $C_s$, in series with the capacitance of the oxide, $C_{ox}$, which can be
described as:

\[ C_{tot} = \frac{C_s C_{ox}}{C_s + C_{ox}} \]  \hspace{1cm} \text{Eq. 1.} \\

\[ \Delta V \] is the shift in voltage created by the polarized layer.

The contribution from the oxide is constant; it is only dependent on the thickness of the insulator, the area of the gate and relative permittivity of the oxide. On the other hand \( C_s \) is a voltage dependent contribution from the semiconductor, for further details see [20]. For p-type material the corresponding C(V) curve show up as the mirror image in the C-axis of the C(V) curve, accumulation for negative voltages and depletion for positive.

At high frequency the minority carriers can not follow the applied alternating voltage and the formed depletion region will remain when the voltage is further changed. If a lower frequency (below 1 kHz) is used this can happen, and the capacitance will rise again [20].

For the capacitors used in this work the C(V) curve is normally shifted from its ideal value along the voltage axis. The shift is caused by the difference in work functions of the metal and the semiconductor, by charges in the oxide or at the

\[ \begin{align*}
\text{Inversion} & \quad \text{Depletion} & \quad \text{Accumulation} \\
\text{Without } H_i & \quad \Delta V & \quad \text{With } H_i
\end{align*} \] 

**Figure 2.5.** C(V) curve of n-doped Pt-MIS capacitor with and without the presence of hydrogen. \( \Delta V \) is the shift in voltage created by the polarized layer.
surface or by surface states at the interface between the semiconductor and the insulator. When a MIS-sensor is exposed to hydrogen this will introduce extra charges or dipoles in the metal – insulator region, which will cause a shift in the C(V) characteristics, as seen in Figure 2.5. The magnitude of the voltage shift, $\Delta V$, can be expressed as the amount of hydrogen adsorbed at the interface:

$$\Delta V = \frac{n_i \mu}{\varepsilon}$$

where $\Delta V$ is the voltage shift, $\varepsilon$ the permittivity, $n_i$ is the concentration of dipoles at the interface (in the range $7 \times 10^{17} - 2 \times 10^{18} \text{m}^{-2}$ [21] for Pt and Pd-MIS devices), $\mu$ is the effective dipole moment.

### 2.6 Silicon Carbide

Silicon Carbide (SiC) is currently under investigation as a material for use in a variety of semiconductor devices in areas where silicon (Si) can not effectively compete [4]. SiC has great promise for use in high power, high temperature, high frequency and harsh environment due to its wide bandgap, high breakdown electric field, and inertness.

The SiC family of crystal structures, is known as polytypes, do not differ in relative numbers of Si and C atoms, but in the arrangement of these atoms in the layers and the stacking of the layers.

The SiC molecule has a carbon atom in the centre of the mass of a tetrahedron of Si atoms, as shown in Figure 2.6. The polytypes are named according to the periodicity of the different layers. For example one of the most common polytypes is called 6H, which means a hexagonal type of lattice with arrangement of 6 different Si + C layers before the pattern repeats itself. The difference between the polytypes is
the stacking sequence of double layers of C and Si atoms along the c-axis. The SiC can have cubic, hexagonal or trigonal structure. The polytype used in this study has been the n-doped 4H SiC.

Figure 2.6. The tetrahedral bonding of a carbon atom with four nearest silicon neighbors.
3.1. Surface reactions

More than one hundred years ago it was discovered that some materials have the ability to increase the rate of chemical reactions without being consumed or altered. Such materials are called catalysts. The chemical sensors used in this work are based on heterogeneous catalytic reactions with the reactions taking place on the active material of the sensor.

When a gas flow hits a solid surface some of the gas molecules can adsorb on the surface. Two types of adsorptions are generally discussed: chemisorption and physisorption. Physisorption is the weakest where no real chemical bonds are created. The binding to the surface involves weak interactions, such as van der Waals forces. When real bonds are created between the surface and the adsorbates, the adsorption is described as chemisorption. The reverse to adsorption is desorption. The understanding of adsorption and desorption of hydrogen on the Pt surface of the Pt-MIS device is of great importance for the understanding of the chemical sensing mechanism.

The number of molecules that will adsorb on a surface will depend on the number of molecules, F, which hit the surface. This flux of molecules impinging on the surface is given by [22]:

\[ F = \frac{N_A p}{\sqrt{2\pi MRT_g}} \]  

Eq. 3
Where \( N_A \) denotes Avogadro’s constant \([\text{mole}^{-1}]\), \( p \) the pressure \([\text{Pa}]\), \( M \) the molar mass \([\text{kg} \cdot \text{mole}^{-1}]\), \( R \) the molar gas constant \([\text{J} \cdot \text{mole}^{-1} \cdot \text{K}^{-1}]\) and \( T_g \) the temperature of the gas \([\text{K}]\).

It is common to use an adsorption isotherm which relates the applied gas pressure to the coverage of the surface. The simplest one is the Langmuir isotherm \([23, 24]\) which builds on three assumptions:

(I) An occupied site will block further adsorption.

(II) Only one layer can be adsorbed.

(III) The heat of adsorption is constant.

The third assumption can be assumed to be realistic at lower coverages.

The coverage on a surface is defined as the number of surface adsorbates per surface atom:

\[
\theta = \frac{n}{N}
\]  

Eq. 4

were \( \theta \) is the coverage, \( n \) the concentration of adsorbates and \( N \) the concentration of available adsorption sites.

Atoms can bind to different sites on the surface and therefore a full coverage of adsorbates does not necessarily correspond to the same number of molecules as there are surface atoms in a monolayer. The concentration of surface Pt atoms of the substrate is assumed to be \( 1.5 \cdot 10^{19} \text{ m}^{-2} \) for a Pt(111) surface, \([25]\). One monolayer (1 ML) of hydrogen atoms corresponds to \( \theta_H = 1 \) \([26]\) while one full layer of oxygen atoms corresponds to \( \theta_O = 0.25 \) as compared to a Pt-layer \([27, 28]\). The adsorption probability, the sticking coefficient, will in the case of simple gas molecules depend on the coverage.

\[
s(\theta) = s_0 (1 - \theta)^x
\]  

Eq. 5
Where \( s_0 \) is the initial sticking coefficient on a clean surface and \( x \) is the adsorption order. For non-dissociative adsorption \( x = 1 \), and for an ideal dissociative adsorption of a diatomic molecule, \( x \) is equal to 2. \( x \) can in practice, however, be a non-integer value. The adsorption rate per surface adsorption site can be described as:

\[
ra = \frac{F}{N_s} s_0 (1 - \theta)^x \tag{Eq. 6}
\]

where \( F \) is the molecular flux of the gas, \( N_s \) the number of adsorption sites per unit surface area.

The desorption rate is proportional to the coverage:

\[
r_d = \kappa \theta^z \quad \text{where} \quad \kappa = \nu_d e^{-\Delta H_d / kT} \tag{Eq. 7}
\]

Where \( \kappa \) is the desorption rate constant, \( z \) is the desorption order, \( \nu_d \) is the pre-exponential factor, \( \Delta H_d \) is the heat of desorption per molecule, \( k \) the Boltzmann constant and \( T \) the surface temperature.

The net adsorption rate can be written as the difference between the adsorption rate, \( r_a \) (Eq. 6), and the desorption rate, \( r_d \) (Eq. 7.)

\[
\frac{d\theta}{dt} = r_a - r_d = \frac{F}{N_s} s_0 (1 - \theta)^x - \kappa \theta^z \tag{Eq. 8}
\]

The reactions studied in this thesis often follow second order adsorption, as in the case with dissociating diatomic molecules. The steady state equation then becomes:

\[
\frac{d\theta}{dt} = \frac{2F}{N_s} s_0 (1 - \theta)^2 - \kappa \theta^2 \tag{Eq. 9}
\]
At steady state, that is when the net adsorption rate $d\theta / dt = 0$, a relation between coverage and gas flow can be established:

$$\frac{\theta}{(1-\theta)} = \sqrt{\frac{FS_0}{N_s N_d e^{-\Delta H_d/2kT}}}$$  \hspace{1cm} \text{Eq. 10}

### 3.1.1. Hydrogen adsorption and desorption on Pt

Hydrogen adsorption is known not to strictly obey second order adsorption. Earlier we modeled the hydrogen adsorption on Pd as a first order adsorption, while the desorption is considered to be second order as described above [13]. Our results (Paper I) show, however, that it is more accurate to use second order adsorption at least for low hydrogen coverages on both Pd and Pt.

### 3.1.2. Permeation

The sensing mechanism of the MIS-structures is based on the ability of the active gate material (e.g. Pd and Pt) to dissociatively adsorb hydrogen molecules. Since it is the variations in hydrogen coverage at the metal-insulator interface that gives rise to the sensor response, also the permeability of hydrogen within the material or the metal is a prerequisite. For Pd and Pt the permeability of hydrogen is high. In fact the diffusion is assumed to be so rapid that an instantaneous equilibrium between the hydrogen concentration at the metal surface and at the interface is obtained. The diffusion time through a 100 nm Pd film at $T = 200^\circ$C will e.g. be $\sim 10^{-5}$ s [29].

Taking into consideration the metal surface, the bulk, and the interface, the interaction of hydrogen with the Pt-MIS structure can be described as:

$$H_2 \xrightleftharpoons{d_s} 2H_s \xrightleftharpoons{d_b} 2H_b \xrightleftharpoons{d_i} 2H_i$$  \hspace{1cm} \text{Eq. 11}
The small letters \( s \), \( b \) and \( i \) denote hydrogen at the surface, the bulk and the interface respectively, \( a \) and \( d \) are rate constants. In practice the catalytic film is a polycrystalline film, and diffusion via grain boundaries will be more important than through the bulk metal grains.

### 3.2. Hydrogen adsorption at the Pt-SiO\(_2\) interface

#### 3.2.1. Hydrogen coverage

The third assumption stated above when applying the Langmuir isotherm is that the heat of adsorption is constant. It is however not unreasonable to think that already adsorbed species may affect nearby adsorption sites. Our experimental results show that there is a linear relation between the C(V)-shift, i.e. the sensor signal, and the logarithm of the applied hydrogen pressure [30]. Assuming that the response is proportional to the hydrogen coverage at the interface, the result indicates that the adsorption of hydrogen at the interface may be described by a Temkin isotherm. Temkin’s model assumes that the heat of adsorption varies linearly with coverage.

\[
\Delta H_i = \Delta H_{i0}(1 - \alpha\theta_i) \quad \text{Eq. 12}
\]

\( \Delta H_{i0} \) is the heat of adsorption of an empty interface and \( \alpha \) is a constant. In this work \( \alpha = 1 \) is used [13]. The transfer rate for hydrogen from the Pt surface to the Pt-SiO\(_2\) interface can be written as [13, 29]:

\[
r_{in} = a_b n_s (1 - \theta_i) \quad \text{Eq. 13}
\]

Where \( \theta_i \) is the hydrogen coverage at the interface and \( n_s \) the number of adsorbed hydrogen atoms per surface area. The rate constant, \( a_b \), can be written as [29]:
where the pre-exponential factor is set to $\nu_{ab} = 10^{13} \text{ [s}^{-1}\text{]}$ [13, 29], and $\Delta H_b$ is the heat of absorption in the bulk. The rate of hydrogen atoms that are transported from the metal SiO$_2$ interface towards the outer surface can be expressed as:

$$r_{out} = d_i n_i (1 - \theta_s)$$  \hspace{1cm} \text{Eq. 15}$$

where $n_i$ is the hydrogen concentration at the interface. The rate constant is [29]:

$$d_i = \nu_{di} e^{-(\Delta H_i - \Delta H_b) / kT}$$  \hspace{1cm} \text{Eq. 16}$$

where $\nu_{di} = \nu_{ab} = 10^{-13} \text{ [s}^{-1}\text{]}$, The heat of adsorption at the interface, $\Delta H_i$, varies as described in Eq. 15. By combining Eq. 14-16 the coverage of hydrogen at the interface is described by:

$$\frac{d \theta_i}{dt} = \nu_{ab} e^{-(\Delta H_s - \Delta H_b) / kT} n_s (1 - \theta_i) - \nu_{di} e^{-(\Delta H_i - \Delta H_b) / kT} n_i (1 - \theta_s)$$  \hspace{1cm} \text{Eq. 17}$$

Calculations and experiments show that the concentration of hydrogen atoms adsorbed at the surface and at the interface are not equal, $n_s \neq n_i$. By using transition state theory (TST) [32] the expression can be written as:

$$\frac{d \theta_i}{dt} = \nu_{ab} e^{-(\Delta H_s - \Delta H_b) / kT} N^* \theta_s (1 - \theta_i) - \nu_{di} e^{-(\Delta H_i - \Delta H_b) / kT} N^* \theta_i (1 - \theta_s)$$  \hspace{1cm} \text{Eq. 18}$$

where $\nu_{ab} = \nu_{ab}' \frac{N^*}{N_s}$, $\nu_{di} = \nu_{di}' \frac{N^*}{N_i}$ and $N^*$ is the number of sites in the transition state. At steady state, $d \theta / dt = 0$ and we get
\[ \theta_s = \frac{1}{(\frac{1}{\theta_i} - 1)e^{-(\Delta H_s - \Delta H_i)/kT} + 1} \]  

Eq. 19

or

\[ \theta_i = \frac{1}{(\frac{1}{\theta_s} - 1)e^{-(\Delta H_i - \Delta H_s)/kT} + 1} \]  

Eq. 20

3.2.2. Dipole moment

Hydrogen atoms or protons adsorbed at the Pt-SiO₂ interface form a dipole layer. Hydrogen adsorbing at the interface will feel the repulsive electrostatic field of the already existing adsorbed hydrogen coverage. A model based on a simple electrostatic interaction can predict the results that are experimentally found. The model assumes that [33]:

I) The dipoles are confined to a two dimensional space, only forming one dipole layer.

II) The adsorbate - adsorbate interaction can be calculated by considering the dipoles as two parallel homogeneously charged sheets.

When a new dipole is formed at the interface, the charges will feel the electrostatic field already existing between the sheets.

Figure 3.1. A schematic picture of adsorbates forming two charged sheets.
The potential step caused by this dipole layer is determined by the hydrogen coverage at the interface (see also section 2.2).

\[ \Delta V = \frac{n_i \mu}{\varepsilon} \]  

Eq. 24

where \( n_i \) is the hydrogen concentration, and \( \varepsilon \) the permittivity, \( \mu \) is the effective dipole moment.

3.3. Oxygen adsorption

In principal three types of interaction between oxygen and surfaces are generally discussed: molecular oxygen adsorption, atomic adsorption and the production of an oxide [34, 35]. Adsorption of oxygen above -123°C, as is the case in this thesis, results in a surface layer of atomic oxygen [36]. The oxygen adsorption isotherm obeys second order adsorption on both Pd and Pt surfaces.

Due to the hydrogen background pressure, the structure will always have a small coverage of hydrogen adsorbed on the surface and also at the metal SiO₂ interface. By exposing the device to oxygen, this hydrogen coverage will be reduced. The interface will be emptied and the sensor will display a shift in opposite direction compared to hydrogen. Indirectly the Pt-MIS devices are consequently sensitive to oxygen and also to dissociating oxygen containing molecules. Even at atmospheric pressure and in synthetic air, oxygen will influence e.g. the hydrogen gas response for example by blocking of hydrogen dissociation.
4.1. Introduction to nanoparticles

Nanotechnology or nanoscience refers to the fact that novel and unique properties of materials are obtained which are due to the small scale. Of particular importance for chemistry, surface energies and surface morphologies are also size-dependent, and this translates to enhanced surface reactivities. Nano crystalline powders have huge surface areas. Nanoparticles are defined as particles in the 1 – 1000 nm range which may be non-crystalline, an aggregate of crystallites or a single crystallite. When talking about nanocrystals one often refers to a solid particle that is a single crystal in the nanometer size range. Consider, for example, that a 3 nm iron particle has 50% of its atoms on the surface, whereas 10 nm particles have just 20% and 30 nm only 5% on the surface [36].

The word nano origins from Greek and means dwarf. When the particle size reaches down to the nanoscale, the particle itself could be considered as a surface in three dimensions. All material will experience a new set of properties when produced in nanoscale form. Electrical, magnetic, geometrical and optical properties are affected by the particle size. For instance, the grain size can affect the conductivity and the resistivity of the material [38].

Heterogeneous catalysis can be considered as one of the first applications of nanoscale materials. The synthesis of ammonia is an example of this, \[3\text{H}_2(g)+\text{N}_2(g)\rightarrow 2\text{NH}_3(g)\] catalyzed by Fe(s). The process was developed by Fritz Haber and
Carl Bosch in 1909 and, the very first reaction chambers used nanoparticle sized powders of osmium and uranium as catalysts [39]).

Nowadays several methods exist to really see these particles as for example High Resolution Transmission Electron Microscopy (HRTEM), Scanning Probe Microscopy (SPM), Atomic Force Microscopy (AFM). The crystal structure of the particles can be identified by X-ray powder diffraction (XRD) although considerable broadening of the XRD peaks occurs for nano-sized materials. There is concern about the toxicity of nano particles, several researchers believe that these particles can be really dangerous since their size is in the range of proteins and amino acids. When particles with the size of 50 and 10 nm were planted in the lungs of rats it showed that the smallest particles were the most dangerous [40]. The problem about nano particles is that they are so small that they can easily penetrate through human tissue. They can also interact with other substances in a new and unexpected way.

![Size comparison of nanocrystals with bacteria, viruses and molecules.](image)

**Figure 4.1.** Size comparison of nanocrystals with bacteria, viruses and molecules. [37]

With nanoparticles as gate material in field effect sensor devices the number of triple points is expected to increase. Triple points
are points were the gas phase; the insulator and the active gate material are present at the same time as described in chapter 2.3. Furthermore, the selectivity of the sensors depends on the combination of metal and insulator as well as the operation temperature. Metal oxide nanoparticles as the gate material of SiC-FET sensors has potential advantages like the high surface area and the specific properties of small particles. A variety of sensing layers may be explored with the intention to enhance the selectivity.

The gate material in SiC-FETs needs to be conducting and this is even more important for capacitor devices. Because of this ruthenium dioxide (RuO₂), and several other metal oxides (e.g. Cobalt oxide (Co₃O₄), magnesium oxide (MgO), chromium oxide (Cr₂O₃), zinc oxide (ZnO)) which has reasonably high electrical conductivity has been identified as interesting candidate gate material for the field-effect sensor devices. Insulating oxides like Al₂O₃, TiO₂, Ta₂O₅ impregnated with metals or conducting oxides are of course also very interesting.

**Phase structures**

To be able to describe the structure of a chemical compound it is necessary to describe the spatial distribution of the atoms in an adequate way. The spatial order of the atoms is called the crystal structure [41]. How the material is described depends also on the coordination numbers for the anions and cations of the material. Commonly occurring structures of nanocrystalline oxides of the one-to-two stoichiometry are anatase, brookite and rutile. One of the most investigated material belonging to these structures is titanium dioxide (TiO₂), therefore the structures will be described based on this material.

One of the major ores of titanium dioxide is called rutile [42], and this is the most common and the most well known mineral of the three listed above. Rutile is a tetragonal structure, where the oxide ions are hexagonally close-packed and the metal
ions occupy the octahedral sites. In titanium the ions will prefer to occupy octahedral holes in a closed-packed structure. The images below depict the structure of rutile TiO$_2$, see Figure 4.2.

**Figure 4.2** a) 2x2x2 unit cells of rutile TiO$_2$. Black spheres symbolizes titanium and the gray one the oxygen. b) This photo is reprinted from John Betts Fine Minerals [43].

**Figure 4.3.** a) 2x2x2 unit cells of brookite structure of TiO$_2$. b) This photo is reprinted from John Betts Fine Minerals [43].
As the Ti$_4^+$ ions are somewhat too big to fit into the octahedral holes, it causes the structure to expand so that the oxide ions are not in contact with each other.

Brookite is an orthorhombic mineral, see Figure 4.3, which at about 750°C automatically revert to the rutile structure. However due to structural differences brookite and rutile differ in crystal habit and cleavage. Brookite shares many of the properties of rutile such as color and lustre and some properties, hardness and density are nearly the same [44].

Anatase or octahedrite is a tetragonal mineral, which about 915°C automatically revert to the rutile structure. Anatase, see Figure 4.4. is the rarest mineral of the three and has the many properties in common with rutile such as lustre, hardness and density, although due to structural differences anatase and rutile differ in cleavage [45].

![Figure 4.4. a) 2x2x2 unit cells of anatase structure of TiO$_2$. b) This photo is reprinted from John Betts Fine Minerals [43].](image)

Anatase and rutile both have tetragonal symmetry but different structures. In rutile, the structure is based on TiO$_6$ octahedrons sharing two of their edges with other octahedrons forming chains. In anatase, the octahedrons share four edges hence the four fold axis [46]. Brookite, as well as anatase (octahedrite), are relatively rare minerals.
Perovskite is the most widespread structure and frequently adopted by phases with the ABO$_3$ stoichiometry. Several hundreds of materials adopt the perovskite structure. In the notation ABO$_3$ the A cation is conventionally the larger of the two metal ions, in SrTiO$_3$ the strontium (Sr) would be denoted A and the titanium (Ti) as the B cation.

Another well known structure is the spinnel, which is widely adopted by ternary oxides and sulphides of the stoichiometry AB$_2$X$_4$. The X denotes oxygen (O) or sulphur (S), A and B are cations, where B applies to a cation type which is twice as abundant in the structure. The two cations are of similar size in contrast to the perovskite structure. Examples of spinell structures are MgAl$_2$O$_4$, TiMg$_2$O$_4$, ZrCu$_2$S$_4$ and Na$_2$WO$_4^+$. Several hundreds of such phases are known.

4.2. **Generation of particles**

Nanoparticles have been synthesized as new sensitive materials for gas sensors. Two methods to generate particles have been used in this thesis, wet synthesis and aerosol deposition, described below. Other techniques like flame spray synthesis, spray pyrolysis and the sol-gel spin coating method have also been used to produce nano-dimension particles with specific gas response properties [references in Paper III].

4.3.1. **Wet synthesis**

In the wet synthesis the chemicals needed are mixed as liquids and then a series of procedures such as changing pH and temperature take place to finally deliver a powder. In this way nanoparticles of ruthenium and ruthenium oxide have been manufactured. The method is described in paper III and IV.
4.3.2. Aerosol technology

Aerosol is used to denote small particles (solid or liquid) suspended in a gas, where the particle size range from nanometer scale to roughly 100 micrometers [48]. Aerosol can be formed as the result of a wide variety of processes that can be classified as physical or chemical [49]. Physical routes include processes where the composition of the material is the same before and after processing, such as nucleation and condensation of a hot vapor during cooling as well as spraying and abrasion. Chemical routes include processes where the final particles are formed as the result of chemical reactions, that is, the composition of the precursor is different from that of the final product. The chemical reaction can occur in the gas phase as well as on the surface, or inside the particles.

4.3.3. Principles for generation of aerosols particles

There are several principles for particle synthesis that can be applied in the particle-film generating system. The choice will depend on the desired properties of the particle film. The techniques can be applied in parallel or sequentially in order to produce materials that are mixed, coated or simply a substrate that will be exposed to different salts for modification purposes. Below follows a short description of some techniques that can be used.

Spray Atomization. The application of sprays is not new, in modern society almost every industry and household uses some form of sprays.

Spray atomization and deposition is a fast growing material processing technique. Soluble components can be formed into particles by producing a spray of droplets from a precursor solution. Each droplet is then dried to form a solid particle. By heating the spray further, the solid particles can be evaporated in order to produce a precursor, see Figure 4.5.
**Gas to particle conversion by physical route.** The gas to particle conversion by physical routes is accomplished by evaporation of one or several compounds in a tubular furnace. The maximum temperature in the reactor is 1500 °C. Particles are formed as the gases are cooled-down along the heating section of the reactor. The particle morphology and size distribution will depend on the operating parameters, e.g. precursor concentration, temperature gradients, and type of flow (turbulent/laminar). The system is suitable for producing particles of more relatively volatile solid precursors, such as metal salts, see Figure 4.6.

**Figure 4.6.** System for conversion of particles by chemical route.
Gas to particle conversion by chemical route. The hot wall reactor is used in order to produce particles by chemical reaction or decomposition of a gas to form a more refractory compound. After the chemical reaction the molecules nucleate to form clusters that grow by coagulation and condensation to form primary particles.

The primary particles then collide to form agglomerates. As with the physical route, particle characteristics depend on the operating parameters. The system needs to be fed with a gaseous or volatile precursor. The composition of the particles will also depend on the composition of the carrier gas, see Figure 4.7.

![Diagram of particle formation](image)

**Figure 4.7.** System for conversion of particle by physical route.

4.3.4. Particle deposition

There are a variety of aerosol methods to form films. These include forming solid particle in a gas, and then depositing the particles onto a substrate, aerosol-assisted chemical vapour deposition (CVD), which uses volatile reactants that evaporate from the solid particles or droplets into the gas phase. The material is then deposited onto a substrate by CVD and the material is formed through chemical reactions on the surface [49].

Deposition of nanoparticles can be made by diffusion onto the substrate that is positioned inside the reactor. The particle size and film structure will depend on where in the reactor the sample is placed. Particle film formation can be enhanced by using an electrostatic precipitation device. In the electrostatic precipitator
(ESP) the gas molecules are ionized by the high electric field density at the discharge electrode. The charged aerosol particles are transported towards the collection plates. A film is obtained by positioning the substrate on the top of the collection plate. Since particles of different sizes will have different mobility in the ESP, size separated deposits can be obtained, see Figure 4.8.

![Figure 4.8. Size separated deposits.](image)

One of the most accurate ways available for obtaining well-defined size selective deposits is to use a Differential Mobility Analyzer (DMA). The DMA separates the poly-disperse aerosol into narrow-size channels by means of the mobility of charged particles in an electric field. The major drawback of the DMA method for film production by nano-particles is the very low particle concentration at the mono-disperse outlet. The low mass yield is a general drawback of the aerosol route to form nanostructures. The properties of the resulting particle depositions from the aerosol process will depend on several operating parameters e.g., the concentration of precursors used, the reactor temperature profile, the residence time, the applied carrier gas composition and the position of the sample. By varying the operating parameters particles with the desired physical properties can be produced. These properties include primary particle size, particle morphology, size and type of agglomerates, crystal structure, distribution of compounds in mixed particles etc.

With aerosol assisted multilayer deposition technique each layer of nanoparticles can be given a specific composition and particles size distribution in order to build up multilayer films with
unique properties. With the aerosol method thin (10-100 \text{ nm})
uniform depositions of particles can be made, without affecting
the layers beneath. This maybe utilized for field effect sensors
such as introducing a bottom layer that will interact with the
insulator and layers on top which act as molecular sieves or as
catalytic selective guards.

In order to use non-conducting materials the deposited
particles need to be modified; this can be done by either
impregnation of suitable salts or by deposition of a salt, a metal or
any conducting material.
NANOPARTICLES
5.1 Processing of the sensors

Two kinds of semiconductor materials, Si and SiC, have been used in this thesis. Different processing is needed for the sensors based on the different semiconductors.

Sensors processed for paper I and II are made from p-doped Si wafers. The wafers were cleaned in H₂SO₄ and H₂O₂ which removes organic and inorganic contamination. HF was used in order to remove the native oxide. After cleaning, the wafer was thoroughly rinsed in deionized water and afterwards dried with N₂. The oxidation of the wafer was done in dry oxygen at 1100°C for approx 40 min forming an oxide of approximately 100 nm. The transport in and out of the oven was made slowly to avoid defects. The oxide on the backside of the wafer was removed with HF. On the backside of the Si wafer, Al was deposited and afterwards annealed at 400°C in H₂ in Ar for 10 minutes to form ohmic rear side contact to Si. A small (1x3 mm²) electrical contact made of Ti and Au (5 nm Ti, 100 nm Au) was evaporated onto the oxide. The catalytic metals (Pt and Pd) were grown by ultra high vacuum electron beam evaporation through Cu shadow masks. The film areas are 8x8 mm with a total thickness of approximately 100 nm. The samples used in paper II
are somewhat different having e.g. different kinds of insulator material, see paper II.

The sensors processed for paper III-VI are made from n-doped 4H-SiC wafers. First a thermal oxide of SiO$_2$ was grown onto the n-doped 4H-SiC surface, followed by a densified layer of Si$_3$N$_4$, which also gives a top layer of SiO$_x$ upon oxidation. The total thickness of the insulator is 80 nm. The Si$_3$N$_4$ was chosen to improve the device performance. Because of the stronger bond between Si-C, as compared to Si-Si that has to be broken during oxidation it takes a higher temperature to grow a certain thickness of SiO$_2$ on SiC as compared to Si [50]. The SiC is electrically connected via an ohmic contact on the rear side, consisting of alloyed Ni (950°C for 30 min in air) with 50 nm TaSi$_x$ and 400 nm Pt deposited on top (as a corrosion protection layer). As bonding pad on top of the sensor a Ti/Pt (5 nm/200 nm) layer was formed.

The active gate region of Ru and RuO$_2$ was formed by drop deposition of particles in a suspension of methanol and deionized water using a micropipette. A constant volume (3 µl) of the suspension was used to define a gate area of ~1 mm diameter for each capacitor. Post-deposition annealing (400°C for 30 min) was performed to enhance the stability of the particles on the SiO$_2$ surface. This thermal treatment was found also effective for consistent electrical behavior of the gate material.

For the sensor in paper VI the SiC sample, processed as above, were placed in the reactor for deposition of the aerosol particle gate material through a Cu shadow mask followed by impregnation of catalytic metal by drop deposition and annealing (400°C, 30 min).
5.2 **Patterning**

In general patterning of sensors is a critical subject. Here we use patterning to manufacture contacts and to form the active gate. The most common method in this thesis is patterning with a shadow mask, which is put on top of the sample, shadowing the parts where we do not want the evaporated material. Thereafter the metal or e.g. a metal oxide is evaporated. In this way bonding pads, contacts and gates are formed. Lift off technology where the desired pattern is formed in a resist layer is used because a very small line width and mass-production is possible. However, the method requires a good adhesion of the desired films to the substrate.

In the case of nanoparticles several techniques were tested. The patterning by shadow mask was not suitable since the particles were in a suspension. When the mask was removed the requested areas followed the mask and thereby the particles did not stay on the surface. The adhesion of the particles was not good enough for using lift off technology. Another often used technique that was tested was stamping with PDMS-stamp (polydimethylsiloxane). Stamps are common in high-resolution soft lithography because they carry the pattern on their surface and are capable of conformal contact during printing. In this way this method could be suitable for patterning with nanoparticles, however in our case we could not get enough nanoparticle material deposited.

The method that worked for deposition of nanoparticles was to drop deposit a suspension of the particles in ethanol/water (1/3) with a micropipette onto the surface and then dry the sample at 100°C followed by an annealing at 400°C. One of the advantages of the particles made by aerosol technology is the good adhesion of the gate material when produced in the reactor.
5.3  **Sample mounting**

It is necessary to mount the samples before performing measurements. Two totally different routes have been used for the set-ups in paper I, II and III-VI, respectively.

5.3.1  *Samples in the ultra high vacuum chamber*

The samples used in the Ultra High Vacuum studies (in Paper I) were placed on a metal plate and contacted by a spring on the front side and by the Al on the backside. The sample was then placed on a stainless sample holder in the chamber, further details, see section 5.5.1.

5.3.2  *Samples measured at atmospheric pressure*

A Pt-100 element together with the sensor chip was glued onto a ceramic micro-heater and placed on a 16-pin holder (Figure 5.1). The Pt-100 element was used for temperature control, and for electrical connection of the sample gold wire bonding is used.

The holders were mounted in leak tight aluminum housing, which are connected to a gas flow line. The gases were primed across the sensor surfaces using a computer-controlled gas mixing system.

This mounting was used for the samples in paper III-VI. For the samples in paper II a somewhat different heater, holder and housing was used.
5.4 Pretreatment

The samples for the UHV studies were transported in laboratory air to the experimental UHV chamber, where the load lock system makes it possible to change samples without having to bakeout the chamber in between. Ar-sputtering and sequential oxygen-hydrogen exposures at temperatures between 200°C and 250°C clean the surface on an atomic scale [14]. To control the cleanliness of the surface UPS and Kelvin probe measurements (see section 5.5.2) were used. In Figure 5.2 a UPS spectra of a clean Pt-MIS surface and of a Pt-MIS surface with adsorbed oxygen are shown.

The UPS spectrum from the platinum surface with and without oxygen agrees well with the spectra obtained by e.g. Gland et. al. from a Pt(111) surface [36]. This pretreatment has been used for the samples in paper I.

The pretreatment of the samples in paper II was somewhat different. These samples were annealed in air at 400°C for 24 h or at 400°C for 24 h with a 250 ppm H₂ in Ar flow through the system. Before measurements the samples were held at 140°C in synthetic air followed by a long pulse of 1 % H₂ in synthetic air.

Figure 5.1. Mounting of the MISiC capacitor sensors, (1) 16-pin holder, (2) sensor chip, (3) ceramic heater, (4) Pt-100 temperature detector.
The nanoparticles are first heat treated in order to get the adhesion of the particles as good as possible and to stabilize the particles. The samples are dried at 100°C, so that the water and the alcohol vanish, and thereafter the sample is heated to 300°C for 30 min. The samples were then calcined at 400°C for several hours in an oxidizing environment and then exposed to a reducing ambient for about the same time. This treatment was performed to stabilize the particle film.

Pretreatment at the start of the measurements of the samples used in paper III-VI are always made the same way. The samples are held at 300°C for 8h in a constant flow of synthetic air, thereafter exposed (for 3h) to pulses of 1% H₂ in synthetic air or synthetic air, each pulse is 20 min long. This is to stabilize the devices and to have a stable baseline.
5.5 Experimental equipment

5.5.1 Ultra high vacuum chamber

The ultra high vacuum stainless steel chamber is shown in Figure 5.3. A base pressure of around $1 \times 10^{-11}$ Torr can be reached. The pumping system consists of two different turbo molecular pumps, a diffusion pump and a combined ion and titanium-sublimation pump. Valves can separately seal off the two different turbo molecular pump stages.

![Figure 5.3. A Schematic picture of the UHV chamber, at two different levels.](image)

Changing of samples is made through a load lock system which makes it possible to change samples without bakeout in between. The gas pressure in the UHV chamber is measured with a hot and a cold cathode ionization gauge.

Heating is done resistively with a coil of Thermocoax and the temperature is measured with a thermo-couple and a Pt-100 element. Thermocoax heating elements consist of one or two
screened electrical resistance wires. The sample holder is mounted on a manipulator allowing three dimensional motion and rotation.

5.5.2 Analytical equipment available in the ultra high vacuum chamber

Analytical tools available in the ultra high vacuum chamber are two mass spectrometers for desorption studies and pressure control, a C(V)-measurement set-up for monitoring the sensor signal, a Kelvin probe for work function measurements and an ultraviolet photoelectron spectroscopy equipment for surface analysis. Other techniques available are electron energy loss spectroscopy (EELS) and X-ray photoemission spectroscopy (XPS). The two latter have, however, not been used in this work.

The system has, as mentioned above, two **quadrupole mass spectrometers**, QMS, one used for desorption measurements (Vacuum Generators SPX300) and the other (Balzers QMA125) for control of the hydrogen partial pressure and of the residual gases. The MS used for desorption measurements is situated so that the sample can be placed nearby, facing the ion source. In this way it is possible to ensure that the registered desorption mainly originates from the investigated surface and not from other processes in the chamber. (This can easily be checked by turning the surface away). The second MS makes it possible to keep the partial pressure of introduced gases constant (within a few percent).

The function of a mass spectrometer is to quantitatively analyze the composition of a gas by ionizing the gas molecules and accelerating them through a mass filter that separates the ions according to their mass/charge \((m/e)\) ratio. Both mass spectrometers that have been used are based on the quadrupole mass filter technique. The mass spectrum is obtained by scanning the voltage, and thereby the \(m/e\) ratio.
In this work the study of desorbing species is crucial. This is done by following one or a few mass peaks as a function of time. All pressures and fluxes used in this thesis are calculated from pressure readings of the hot cathode ionization gauge using sensitivity factors published by e.g. Nakao [51]. The factors that have been used are 0.44 for hydrogen, 0.40 for deuterium and 0.87 for oxygen.

The work function is the least amount of energy required to remove an electron from the surface of a conducting material to a point just outside the metal with zero kinetic energy. The work function is an extremely sensitive indicator of the surface condition. The Kelvin probe is a non-contact, non-destructive vibrating capacitor device used to measure contact potential difference. The probe is attached to a piezoelectric crystal, making it possible for the probe to vibrate. Due to the vibration of the probe and to the contact potential difference between the probe and the sample surface, an AC current will flow between the contacts [52]. This current is used to measure work function changes during the experiments. Note that only work function changes can be measured with this equipment, not the absolute value of the work function. Changes in the coverage, bonding, and structure of adsorbates on surfaces are accompanied by a change in the surface work function.

One well known method to investigate what kind of species that are present on a surface is ultra violet photoelectron spectroscopy (UPS). In UPS the sample is exposed to monochromatic ultraviolet photons which exciting electrons are detected and energy analyzed. Here the ultraviolet light is obtained from a Helium lamp emitting at 21.2 eV (He I radiation) or 40.8 eV (He II radiation). The helium radiation has low energy, which means that deep core electron levels cannot be excited. The electrons that are emitted origin from the valence band. By
studying these emitted electrons it is possible to map the initial electron states. UPS gives information on the bonding of adsorbates to the surface \[53\]. Here the technique was primarily used to determine the cleanliness of the surface.

5.5.3 Equipment for electrical characterization in UHV

To evaluate changes in the electric properties of the MIS device in UHV an experimental set up \[15\] to control the voltage needed to keep a certain capacitance constant (= the C(V)-signal) is used. The temperatures used in this thesis ranges from 50°C to 250°C and the frequency used in our case is 33 kHz.

5.5.4 Multi capacitance meter

For C(V)-studies at atmospheric pressure (papers II-VI) a set-up where the sensor is kept in a container with a constant flow of gas is used. The sample is heated with a heating plate and the temperature used is in the range of 100-400°C.

The sensor chip holds up to 5 devices and it is possible to connect 3 housings at a time. The carrier gases used in the atmospheric measurements are synthetic dry air (20% O₂ in 80% N₂) O₂ and N₂. Various concentrations of H₂, NH₃, CO, NO, HC are used either in synthetic air or in N₂. Mixing is provided by a gas mixing system, see below. A Boonton capacitance meter, model 7200, has been used to measure the C(V)-characteristics; the Boonton meter uses a frequency of 1 MHz. A multiplexing system enables measurements of the voltage at a constant capacitance for time resolved gas sensing of up to 15 samples.

To enable C(V)-measurement at different frequencies a Hewlett Packard 41924 LF impedance analyzer was used. The capacitance-voltage (C(V)) characteristics were obtained in the
frequency range 500Hz – 1 MHz. This allows us to investigate the
devices in more detail. At high frequencies defects in the
semiconductor will affect the devices and at lower frequencies the
effects of minority carriers play an important role.

5.5.5 Gas mixing

The gases at atmospheric measurements were provided by a
gas mixing system, the typical gas flow was 100 ml/min. It is
possible to dilute gases so that a series of concentration of test
gases can be tested. The test gases used are hydrogen (H₂),
ammonia (NH₃), propene (C₃H₆), nitric oxide (NO) and carbon
monoxide (CO). Normally the carrier gas was dry synthetic air
(20% O₂ and 80% N₂), but pure nitrogen (100% N₂) has also been
used as carrier gas.

5.6 Other analytical techniques and measurement set-ups

5.6.1 Auger electron spectroscopy

Auger Electron Spectroscopy (AES) is a surface analytical
method used to identify surface composition. The Auger process
(named after Pierre Auger) is non-destructive and it is only from
the first few atomic layers of a solid surface that the information
is obtained. Repeated sputtering of the surface layer is used for
depth profiling.

The sample is irradiated by an electron beam with a well
defined energy in the 2-25 keV range. A core electron is excited
creating a hole in the electron orbital. This hole is subsequently
filled by an electron from an outer shell, which may transfer its
excess energy to another outer shell electron (or as photon). This
last electron, the Auger electron, is then emitted. The energy of
the Auger electron is characteristic of the element that emitted it, and can thus be used to identify the element.

5.6.2 Atomic force microscopy

Atomic force microscopy (AFM) is a technique for analyzing the morphology of a surface. A mechanical probe oscillates close to the sample surface and a feedback mechanism maintains the tip at a constant force between tip and sample as the movement of the tip is stored. In this way it is possible to obtain high resolution topographical information. The data output is either a three dimensional image of the surface or a line profile with height measurements. AFM typically does some damage to the sample but it is convenient to use since it can be operated in air.

In this work we have used AFM to investigate the reconstruction of the catalytic metal. The Pd metal film undergoes severe changes during pretreatment while Pt films show almost no such changes, see paper I. The reconstruction of the Pd and Pt films has been studied in more detail [54-56]. The metal films, especially Pd, undergo surface reconstruction during the experiment, as shown by AFM studies on samples that are fresh and samples used in UHV experiments. A study was made to look at this in more detail. A series of Pt and Pd MIS devices were heated to different temperatures.
The study revealed that Pd starts to undergo morphology changes already at 100°C and severe changes are noted when the sample is heated to 400°C, while the same effect on Pt is not seen until 600°C, see Figure 5.4. It should be noted that the measurement situation in UHV and at atmospheric conditions as in ref. [56], where reconstruction of Pt is reported at lower temperature, are substantially different for example regarding surface coverage of gas species.

5.6.3 Scanning electron microscopy

A focused electron beam scanned across the surface creates images in the scanning electron microscopy (SEM). Low energy secondary electrons emitted and detected. Other signals, as X-rays
and high energy backscattered electrons, can also be detected. This makes it possible to determine the elements present in the selected region. If low energy secondary electrons are collected a surface topography is obtained. Information about surface roughness, porosity, granular deposits, and stress-related cracks can be obtained and even observations of grain boundaries are obtained. SEM is a fast, near-surface screening method that gives you a better depth profile than normal optical microscopy does. Conductive and nonconductive samples can be imaged.

5.6.4 Transmission electron microscopy

In transmission electron microscopy (TEM) a focused beam of electrons is passed through a very thin item and results in an image projected onto a fluorescent screen. Where an electron passes through a specimen, the image of them is white, and where the electrons have been blocked by the specimen, the image is dark. Specimens are typically ultra thin sections of material, small objects (viruses, proteins and nanoparticles), or thin replicas of a surface.

5.6.5 X-ray photoelectron spectroscopy

In X-ray photoelectron spectroscopy (XPS), also known as Electron Spectroscopy for Chemical Analysis (ESCA), X-rays bombard the sample creating ionized atoms and ejecting free electrons. The energies of these free electrons are related to their binding energies in the original molecule or atom. By measuring these energies one can identify the chemical elements present in the sample. XPS provides both elemental and, to a certain extent, chemical information in the top 3-30 atomic layers (10-100 Å) in solid samples. Measurements can be made at greater depths by ion
sputtering to remove surface layers. XPS is especially good for obtaining elemental surface composition of unknown materials, including conductors and insulators.

XPS is a nondestructive technique which makes it very important. For example it is possible to study changes in the oxidation state of a molecule. This is because the oxidation causes changes in the energies of the electrons that are ejected and this can be analyzed. These energy shifts (sometimes called chemical shift) have been studied and tabulated for many different compounds which make it possible to distinguish between different states.

5.6.6 Diffuse reflectance infrared Fourier transform spectroscopy

Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectroscopy is an alternative Fourier Transform Infrared Spectroscopy (FTIR) method where the diffusely reflected radiation is measured. In this technique, the IR radiation that is scattered from the irradiated sample is collected by mirrors and detected. The DRIFT mode is more suited for studying solid materials since powders can be measured without special sample preparation. The light undergoes multiple reflections on particle surfaces, whiteout penetrating into the particle.

DRIFT offers a number of advantages as a sample analysis technique including almost no sample preparation, ability to analyze most non-reflective materials, very high sensitivity down to low ppm level and ability to analyze irregular surfaces or coatings. The technique can be used to identify contaminants, organic stains and in surface studies to reveal information about adsorbates on the surface e.g. The DRIFT studies can be performed while heating the sample and during gas exposure, that is very close to realistic conditions.
X-Ray Powder Diffraction (XRD) is a technique used for analyzing the basic structural properties of crystalline and semi-crystalline materials. XRD is a powerful non-destructive technique for characterizing crystalline materials. It provides information on structures, phases, preferred crystal orientations (texture) and other structural parameters such as average grain size, crystallinity, strain and crystal defects. The technique is based on the well known Bragg reflection [22], according to Braggs law.

Powder diffraction patterns are characteristic of the spatial relationship of molecules in a crystalline lattice and can be used to identify the components of a material or to correlate its physical properties to solubility, strength, or appearance.

The peak intensities are determined by the atomic decoration within the lattice planes. Consequently, the X-ray diffraction pattern is the fingerprint of periodic atomic arrangements in a given material. An on-line search of a standard database for X-ray powder diffraction patterns enable quick phase identification for a large variety of crystalline samples.

The applications of the technique are for instance qualitative phase identification, characterization of amorphous or crystalline structures, impurity analysis and study of phase transformation. Also the average grain size of nano crystalline products can be made with XRD.

The contribution due to grain size can be estimated with the Scherrer formula [57]:

5.6.7 \textit{X-ray diffraction}
\[ B_{\text{grain}} = \frac{K\lambda}{D \cos \theta} \]  

Eq. 25

where \( K \) is the Scherrer constant (=0.9) and \( D \) (from the width of the peak) is the grain dimension measured in direction perpendicular to a particular set of reflecting planes, \( \lambda \) is the wavelength of the X-rays and \( \theta \) the incident angle.
6.1 Comparison of Pt and Pd in MIS devices in ultra high vacuum studies

From the studies in UHV we learned that the MIS devices based on the two catalytic metals Pt and Pd are similar but that there are some qualitative differences. Detailed studies on Pd show that the hydrogen adsorption should be considered as second order, at least at relatively low coverages. The interface adsorption is concluded to follow a Temkin isotherm, where the hydrogen adsorption potential varies with hydrogen coverage. Fitting a theoretical model to the experimental results produces values for the heats of adsorption both at the Pd and Pt surfaces, $\Delta H_{s}(Pd) = 0.41$ and $\Delta H_{s}(Pt) = 0.45$ eV/hydrogen atom, and at the Pd-SiO$_2$ and Pt-SiO$_2$ interfaces, $\Delta H_{\delta}(Pd)=0.86$ and $\Delta H_{\delta}(Pt)=0.78$ eV/hydrogen atom.

Further more the concentration of adsorption sites at the metal insulator interfaces is considerably smaller than the concentration of adsorption sites on the outer surface. The concentration of adsorption sites at the interface is found to be almost three times less for Pt than for Pd in the present study.

The interface hydrogen atoms are, however, strongly polarized, so even though the concentration of hydrogen atoms at the interface is small, the sensor signal can be significant. The dipole moment is estimated to 0.6-0.7 D. The Pt-MIS device is sensitive to hydrogen pressure changes down to the $10^{-12}$ Torr scale.
6.2 A study of different insulators in MIS devices

The surface chemistry of the insulator of MIS field effect gas sensors influences the gas response; this is shown in paper II. The results support a response mechanism where the hydrogen trapping sites are located at the oxygen atoms of the insulator surface. The oxygen concentration of the insulator surface determines the size of the saturated response.

Depending on the type of insulator that is chosen, differences in the sensitivity properties are achieved. The oxygen concentration at the insulator surface plays a major role. In particular the detection limit for devices with Ta$_2$O$_5$ appears to be lower than for the other insulators, indicating a higher trapping energy for this insulator surface. Si$_3$N$_4$ tends to oxidize through a porous metal layer and the device becomes with time very similar to the device with SiO$_2$ as the insulator. No saturation of the hydrogen response is observed below 1% H$_2$ for devices with Al$_2$O$_3$ as insulator material. For SiO$_2$ and Si$_3$N$_4$ saturation is observed at around 1000 ppm H$_2$.

6.3 Nanoparticles wet synthesized in SiC-MIS devices

We consider catalytic active nanoparticles as potential candidates to be used as the gate material for high temperature, long-term stable FET sensor devices. In paper III-V we have tested some new materials, such as wet synthesized nanoparticles of RuO$_2$ and Ru. Challenging problems when using nanoparticles as the gate material in FET devices are poor adhesion and low conductivity in the films. The latter is a result of too low density of conducting particles or impregnated metal particles. A major result in this work is that a functioning process has been developed for processing and testing of wet synthesized nanoparticles as gate material in gas sensitive MISiC-FET devices.

A film of RuO$_2$ nanoparticles was employed as gate material in capacitive devices and showed sensitivity to reducing gases. The sensitivity pattern depends on the operating temperature of the
device. The maximum operating temperature for a Ru capacitor is at 200°C and at 300°C for a RuO₂ capacitor, consistent with the catalytic activity e.g. for the water production of these materials. This is comparable to the Pt-gate and Ir-gate field effect sensor that has a maximum operating temperature at 200°C and 300°C, respectively [2].

Preadsorbed oxygen together with oxygen vacancies are identified by theoretical modeling as important parameters in the sensing mechanism for the water production. The use of a metal oxide as gate material gives interesting suggestion for the detection mechanism through the comparison to porous metals as gate material on SiO₂.

6.4 Aerosol deposited nanoparticles in MISiC-FET devices.

Aerosol deposited particles such as SiO₂, TiO₂, Al₂O₃ impregnated with catalytic metal, in this case Pt, gives conducting and porous layers that are sensitive to hydrogen. The aerosol deposited nanoparticles show better adhesion as compared to the wet synthesized particle deposited by drip technology.

The C(V) characteristics of these gate materials are comparable to those of RuO₂ capacitors. The resistivity of the deposited materials is ~700Ω, which is somewhat too high. To lower this value more metal needs to be added. This can easily be made by repeating the impregnation by metal acid solution.
RESULTS
FUTURE WORK

To be able to investigate fundamental properties such as the concentration of active sites at the interface, activation energies and reaction pathways that influence the response of MIS gas sensors, studies performed in ultra high vacuum are needed. So far only Pd and to some extent Pt has been investigated as gate material. The difference between Pt and Pd revealed in this work makes it interesting to also study for example iridium (Ir) and rhodium (Rh) as well as the conducting metal oxides like RuO$_2$ and metal impregnated metal oxides, e.g. Pt-Al$_2$O$_3$, Pt-TiO$_2$ and so on. Continuous films should be compared to porous films and films of nanoparticles.

Combination of UHV studies with computational calculations may give interesting results. This can track the reaction pathways that are involved in the sensors response mechanism and thereby also provide the basis for better algorithms for calculated predictions of the sensor response.

Using nanoparticles as gate material is a new research field that has just started. It is almost only the imagination that puts limits to what can be done, but of course there are practical issues that have to be solved.

To start with more work has to be done on the impregnation method. Now this is performed in a non specific way and the amount of metal differ between the samples. To be able to deposit already metal impregnated non-conducting metal oxide particles with the aerosol technique is an interesting way to solve this problem. Since the aerosol deposited particles has a better adhesion this is also a way to solve that major problem.
There are many new material combinations that are interesting to explore. One possibility is to deposit layer by layer in sandwich type structures of different aerosol nanoparticles. Perhaps annealing can be used afterwards to mix the layers.

The aerosol deposition can give particles of a wide range of particle size. Depositing particles with different size and then use these as gate material in MIS devices is another interesting research topic. The size of the particles may affect the preferred reaction pathway on the particle surface. In this way it might be possible to design particles that are selective towards different species even though they are of the same material.

Studies in UHV of nanoparticles are interesting according not only the reactions taking place but also to study changes in the particles and the influence of this on the gas response.

Other analytical techniques like XPS and XRD will also give important information. One identified technique of special interest is DRIFT spectroscopy. This is normally performed on powder samples. Preliminary results have shown that MISiC-devices with nanoparticles as gate material may realize simultaneous DRIFT and sensor signals. In combination with theoretical calculations this may create valuable knowledge.
REFERENCES


REFERENCES


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This is maybe the most difficult part to write, you are so many and I do not want to forget any of you. This is my chance to thank all of you who has worked together with me, supported me and encouraged me through these years (that turned out to be more than I ever had thought).

**Anita Lloyd Spetz**, whiteout whom this goal would not have been reachable. If you would not have given me a “second” chance, I would never have become a “doctor”. You always listen, come up with new ideas, want to discuss and cares about my work and about me as a person. Anita; Thank you!

**Helen Dannetun**, you are the one who are responsible for me even starting this journey. I am grateful for your encouragement during the first period of my work. I know that you are as happy as I am that I finally made it.

**Mats Eriksson**, thank you for guidance during the first part of my work. Without you I think that Ultek would have been “killed” even earlier…I would never have managed to keep “him” alive as long as I did.

**Lars Gunnar Ekedahl** and **Ingmar Lundstöm**, for always supporting the work within the group and for always being there guiding and willing to discuss results and ideas.
ACKNOWLEDGEMENTS

Helena Wingbrant, Mike Andersson, Kristina Buchholt, Vedran Bandalo, John Howgate, Judtih Cerdà, Somenath Roy, Henrik Svenningstorp, Lars Unéus, Martin Johansson, Helena Amandusson and Lisa Åbom, dear colleagues and friends who has made the days at IFM funnier and shorter. You are all special to me, both for being the persons you are and for spending the working hours together with me.

Mehri Sanati, Michael Strand and Doina Lutic, my supporting colleagues at Växjö University. It has been nice to get to know all of you! Mehri and Micke you always have time for my questions and listen to my ideas. Mehri, you are the one who gave us the idea about using particles, Thank you!

Per-Olov Käll, Lars Ojamäe and their former diploma workers Christian Aulin and Henrik Pedersen, for bringing chemistry to my world of physics. I appreciate your support. It has been great working with you guys.

Kajsa Uvdal and Rodrigo M. Petoral Jr. Thank you for your skillful help with XPS experiments and evaluation.

All the staffs at IFM working, 1998-2005, without you not much work would have been done. Thank you: Therese D., Bo T., Jeanette N., Evald M. Ingemar G., Hans S., Rolf R., Thomas L.

And finally, Per Salomonsson, thank you for always being there, always taking care of me and believing in me. Without you I would only be half a person. I love you!