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SIC-FET GAS SENSORS DEVELOPED FOR
CONTROL OF THE FLUE GAS
DESULFURIZATION SYSTEM IN POWER PLANTS,
EXPERIMENTAL AND MODELING

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Cover image

The cover image consists of a sensor signal from SO_2 measurement in the presence and absence of oxygen, a SiO_2 cluster, and a Pt_4 cluster interacting with SO_4^{2-} ion.

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Abstract

Electricity and power generation is an essential part of our life. However, power generation activities also create by-products (such as sulphur oxides, nitrogen oxides, carbon monoxide, etc), which can be dangerous when released to the atmosphere. Sensors, as part of the control system, play very vital role for the flue gas cleaning processes in power plants. This thesis concerns the development of Silicon Carbide Field Effect Transistor (SiC-FET) gas sensors as sensors for sulfur containing gases (SO_2 and H_2S) used as part of the environmental control system in power plants. The works includes sensor deposition and assembly, sensing layer characterization, operation mode development, performance testing of the sensors in a gas mixing rig in the laboratory and field test in a desulfurization pilot unit, and both experimental and theoretical studies on the detection mechanism of the sensors.

The sensor response to SO_2 was very small and saturated quickly. SO_2 is a very stable gas and therefore reaction with other species requires a large energy input. SO_2 mostly reacts with the catalyst through physisorption, which results in low response level. Another problem was that once it finally reacted with oxygen and adsorbed on the surface of the catalyst in form of a sulfate compound, it is desorbed with difficulty. Therefore, the sensor signal saturated after a certain time of exposure to SO_2 . Different gate materials were tested in static operation (Pt, Ir, Au), but the saturation phenomena occurred in all three cases. Dynamic sensor operation using temperature cycling and multivariate data analysis could mitigate this problem. Pt-gate sensors were operated at several different temperatures in a cyclic fashion. One of the applied temperatures was chosen to be very high for a short time to serve as cleaning step. This method was also termed the virtual multi sensor method because the data generated could represent the data from multiple sensors in static operation at different temperatures. Then, several features of the signal, such as mean value and slope, were extracted and processed with multivariate data analysis. Linear Discrimination Analysis (LDA) was chosen since it

allows controlled data analysis. It was shown that it was possible to quantify SO_2 with a 2-step LDA. The background was identified in the first step and SO_2 was quantified in the second step. Pt sensors in dynamic operation and 2-step LDA evaluation has also demonstrated promising results for SO_2 measurement in the laboratory as well as in a desulfurization pilot unit. For a commercial sensor, algorithm have to be developed to enable on-line measurement in real time.

It was observed that Ir-gate sensors at 350°C were very sensitive to H_2S . The response obtained by Ir sensors to H_2S was almost five times larger than that of Pt sensors, which might be due to the higher oxygen coverage of Ir. Moreover, Ir sensors were also more stable with less drift during the operation as a result of higher thermal stability. However, the recovery time for Ir sensors was very long, due to the high desorption energy. Overall, the Ir sensors performed well when tested for a leak detection application (presence of oxygen and dry environment). The geothermal application, where heat is extracted from the earth, requires the sensor to be operated in humid condition in the absence (or very low concentration) of oxygen, and this poses a problem. Temperature cycle operation and smart data evaluation might also be an option for future development.

Along with the sensor performance testing, a study on the detection mechanism was also performed for SO_2 sensor, both experimentally and theoretically. The experiment included the study of the species formed on the surface of the catalyst with DRIFT (diffuse reflectance infrared fourier transform) spectroscopy and the analysis of the residual gas with mass spectroscopy. Explanatory investigation of the surface reactions was performed using quantum-chemical calculations. Theoretical calculations of the infrared (IR) vibration spectra was employed to support the identification of peaks in the DRIFT measurement. Based on the study on the residual gas analysis and quantum-chemical calculations, a reaction mechanism for the SO_2 molecule adsorption on the sensor surface was suggested.

Populärvetenskaplig sammanfattning

Gassensorer baserade på kiselkarbid utvecklade för kontroll av svavelreningssteget i värmekraftverk, experiment och modellering

Elektricitet och generering av elektrisk ström är en mycket viktig del av våra liv. Men generering av elektricitet orsakar också biprodukter såsom gaser som innehåller svavel och kväveoxider vilka är skadliga t.ex. när de släpps ut i atmosfären. Värmekraftverk är en viktig källa till både värme och elektricitet. De flesta värmekraftverk eldas med bränsle som innehåller svavel, vilket bildar svaveldioxid under förbränningen i kraftverket. Svaveldioxiden släpps ut i atmosfären via rökgaserna från kraftverket. I atmosfären kan svaveldioxiden orsaka surt regn och svaveldioxid är också ett förstadium till sura partiklar som är farliga för vår hälsa. Svaveldioxiden i rökgaserna måste därför hållas på en låg nivå innan den släpps ut till atmosfären. Detta sker med hjälp av ett speciellt reningssteg som tar bort svavel. En blandning av släckt kalk och aska tillsätts rökgasen, den absorberar svaveldioxiden och sedan filtreras askblandningen bort från rökgaserna och kan återanvändas igen i reningssteget. Med ett sensorsystem som mäter svaveldioxidhalten i rökgaserna är det möjligt att förfinas och optimera effekten av reningssteget.

Den här avhandlingen handlar om utvecklingen av gas sensorer för svavelhaltiga gaser (svaveldioxid och vätesulfid) baserade på kiselkarbid som kan användas vid hög temperatur och i korrosiv miljö som den i rökgaserna i ett värmekraftverk. Dessa sensorer tillverkas med metoder som tillåter masstillverkning och de blir därför billiga och kan placeras på många ställen i rökgaserna, vilket ger bättre kontroll. Styrning med dessa sensorer har därför potential att minska mängden svavel som släpps ut. Arbetet innehåller tillverkning av sensorerna samt tester av dessa både i labbskala och i fältmätningar. Det senare har skett i en pilotanläggning där mängden svavelhaltig gas kan kontrolleras för olika tester t.ex. för att utveckla och optimera reningssteget för svavel.

En annan gassensor som har utvecklats i den här avhandlingen detekterar svavelväte. Detta är en giftig gas som bildas t.ex. när bakterier bryter ner organiska föreningar i jorden. Geotermisk energi är en förnyelsebar energikälla som tar vara på värmen djupt nere i jorden t.ex. genom att pumpa upp ånga från jorden, som sedan genererar elektricitet i en turbin. Den här ångan för ofta med sig svavelväte som måste filtreras bort innan den släpps ut i atmosfären. Den processen behöver kontrolleras med en sensor som detekterar svavelväte. Den behöver detektera mycket låga halter av gasen eftersom den är väldigt giftig redan i små koncentrationer (hygieniska gränsvärdet för svavelväte är 10 ppm / 14 mg/m³). Det visade sig att kiselkarbidsensorerna som har ett känslskikt av iridium kan detektera oerhört små koncentrationer av svavelväte. Dessa sensorer har tillverkats och studerats för detta ändamål.

Det visade sig vara mycket svårare att hitta ett bra känslskikt för att detektera svaveldioxid. Sensorerna som testats ger bara en liten respons på denna gas. Lösningen här blev att använda en kiselkarbidsensor med känslskikt av platina och använda en cykliskt varierande arbetstemperatur. Sensorsignalen tas ut från olika intervall i temperaturcykeln och sedan används statistiska metoder för datautvärderingen. En tvåstegsmetod visade sig fungera bra där sammansättningen av bakgrundsgaserna först identifieras och koncentrationen av svaveldioxid sedan bestäms i ett nästa steg. Lovande tester har gjorts både i labbet och på data genererade av en sensor i rökgaserna på en mindre testanläggning av ett kraftvärmeverk där man kan variera mängden svaveldioxid på ett kontrollerbart sätt. För kommersiellt bruk måste utvärderingsmetoder utvecklas som kan generera gaskoncentrationen från sensorsignalen kontinuerligt när den mäter direkt i rökgaserna.

Studier av vad som produceras på sensorytan när svaveldioxid detekteras har gjorts med infrarödspektroskopi samt med masspektrometer. Dessa resultat tillsammans med teoretisk modellering har använts för att föreslå en modell för vad som sker med gaserna på sensorytan. Denna kunskap skapar möjlighet att vidareutveckla och förfina sensorerna för att detektera svaveldioxid och svavelväte.

Preface

This thesis reports my PhD studies in the Applied Sensor Science group at Linköping University. The results are presented in appended papers. This work was performed as a project in *FunMat*, VINN Excellence Center in Functional Nanoscale Materials, in collaboration with Alstom Power AB for the development of SO₂ and H₂S sensors. The transistor devices were supplied by Sensic AB. The sensor development was accompanied by theoretical modeling, performed together with the physical chemistry group. The theoretical calculation was performed with the resources from the National Supercomputer Center (NSC). The studies with DRIFT spectroscopy were performed in collaboration with the Competence Center for Catalysis (KCK) Chalmers.

During the duration of the PhD study, I was enrolled in Agora Materiae Graduate School.

Part of the thesis is taken from Licenciate Thesis No. 1554, SiC FET gas sensors: theory, development, and applications to flue gas cleaning processes in power plants, published in 2012.

Included papers

PAPER 1

SiC – FET based SO₂ sensors in power generation applications

Z. Darmastuti, C. Bur, P. Möller, R. Rahlin, N. Lindqvist, M. Andersson, A. Schütze, A. Lloyd Spetz

Sensors and Actuators B, Chemical, vol. 194, pp. 511 – 520 (2014)

I was responsible for the planning of the project, performed the SEM and sensing measurement both in the laboratory and in the pilot unit, did the majority of data evaluation and analysis with input from co-authors. I was also responsible for the writing of the manuscript.

PAPER 2

Hierarchical methods to improve the performance of the SiC FET as SO₂ sensors in flue gas desulphurization system

Z. Darmastuti, C. Bur, N. Lindqvist, M. Andersson, A. Schütze, A. Lloyd Spetz

Submitted to Sensors and Actuators B, Chemical

I was responsible for the planning of the project, performed the sensing measurement both in the laboratory and pilot unit, data evaluation and analysis with input from co-authors. I was also responsible for the writing of the manuscript.

PAPER 3

Vibrational analysis of SO₂ on Pt / SiO₂ system

D. Bounechada, **Z. Darmastuti**, L. Ojamäe, M. Andersson, A. Lloyd Spetz, M. Skoglundh, and PA. Carlsson

Manuscript

I was responsible for the planning of the project, involved in the planning of the experiment, performed the theoretical calculations, took part in data analysis, wrote the introduction and the quantum-chemical part of the manuscript.

PAPER 4

Detection mechanism studies of SO₂ on Pt / SiO₂ system

Z. Darmastuti, D. Bounechada, PA. Carlsson, M. Andersson, M. Skoglundh, A. Lloyd Spetz, L. Ojamäe

Manuscript

I was responsible for project planning, performed mass spectroscopy, sensing measurement, and theoretical calculations, data evaluation and analysis with some input from co-authors. I was also responsible for the writing of the manuscript.

PAPER 5

SiC based field effect transistor for H₂S detection

Z. Darmastuti, M. Andersson, N. Lindqvist, A. Lloyd Spetz

Manuscript

I was responsible in planning of the project, involved in the sensor deposition, sensing layer characterization, and assembly, performed the sensing measurement, as well as the data evaluation and analysis with input from co-authors. I was also responsible for the writing of the manuscript.

Related journal and conference papers

SiC-FET based SO₂ sensor for power plant emission applications

Z. Darmastuti, C. Bur, P. Möller, N. Lindqvist, M. Andersson, A. Schütze and A. Lloyd Spetz

Proceedings of Transducers & Eurosensors XXVII (2013) pp. 1150 – 1153 (Related to Paper 1)

Chemical sensor systems for environmental and emission control

A. Lloyd Spetz, **Z. Darmastuti**, C. Bur, J. Huotari, R. Bjorklund, N. Lindqvist, J. Lappalainen, H. Jantunen, A. Schütze and M. Andersson

Proceedings of SPIE (2013) art. no. 87250I

SiC – FET methanol sensors for process control and leakage detection

Z. Darmastuti, P. Battacharya, J. Kanungo, M. Andersson, S. Basu, P.O. Kall, L. Ojamäe, A. Lloyd Spetz

Sensors and Actuators B, Chemical 178, pp. 385 – 394 (2013)

SiC – FET Sensors for methanol leakage detection

Z. Darmastuti, P. Bhattacharyya, M. Andersson, S. Basu, P.O. Kall, L. Ojamäe, A. Lloyd Spetz

Proceeding of 14th IMCS (2012) pp. 1579 – 1582

Development of SiC – FET methanol sensor

J. Kanungo, M. Andersson, **Z. Darmastuti**, S. Basu, P.O. Kall, L. Ojamäe, A. Lloyd Spetz
Sensors and actuators B, Chemical 160(1), pp. 72 – 78 (2011)

SiC based field effect transistor for H₂S detection

Z. Darmastuti, M. Andersson, M. Larsson, N. Lindqvist, L. Ojamäe, A. Lloyd Spetz
Proceedings of IEEE Sensors (2011) pp. 770 – 773 (Related to Paper 5)

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Contents

1	Introduction	1
2	Flue Gas Cleaning Processes and Target Gases	3
2.1	Flue Gas Cleaning Processes in Thermal Power Plant and Sulfur Dioxide as Target Gas	3
2.2	Flue Gas Cleaning Processes in Geothermal Power Plant and Hydrogen Sulfide as Target Gas	6
3	Available Sensor Technologies	7
3.1	Metal Oxide Semiconductor gas sensors	7
3.2	Electrochemical and Solid Electrolyte gas sensors	9
3.2.1	Electrochemical gas sensors	9
3.2.2	Solid Electrolyte gas sensors	9
3.3	Fiber optic and other optical Sensor	10
3.4	Field Effect Transistor gas sensors	11
3.4.1	Operating temperatures	14
3.4.2	Gate and substrate bias	15
4	Dynamic Operation, Signal Processing, and Multivariate Data Analysis	17
4.1	Temperature cycled operation	17
4.2	Signal Pre-processing	18
4.3	Multivariate Data Analysis	19
5	Sensor Fabrication and Sensing Measurement	21
5.1	Sensor Fabrication	21

5.1.1	Deposition of the sensing layer	21
5.1.2	Morphology characterization of the sensing layer	22
5.1.3	Sensor assembly	22
5.2	Performance Testing	23
5.2.1	Laboratory measurement	23
5.2.2	Pilot Unit Measurement	24
6	Detection Mechanism Studies	27
6.1	Experimental Methods	27
6.1.1	DRIFT spectroscopy	27
6.1.2	Mass spectroscopy	28
6.2	Theoretical Calculations	28
6.2.1	Quantum-chemical computations	28
6.2.2	Clusters and surface models	29
6.2.3	Reaction mechanism energy profile	30
6.2.4	Vibrational spectra calculations	32
7	Summary of the Results	33
7.1	Performance of field effect transistor as sulfur dioxide sensor in thermal power plant application (Paper 1 and 2)	33
7.2	Detection mechanism studies of sulfur dioxide on $Pt - SiO_2$ system (Paper 3 and 4)	34
7.3	Hydrogen sulfide sensor in geothermal power generation application (Paper 5)	34
8	Contributions to the Field and Outlook	35
Paper 1		
Paper 2		
Paper 3		
Paper 4		

Paper 5

Introduction

Increasingly stricter regulations concerning polluting emissions from power plants heighten the need for better flue gas cleaning processes. Many new technologies with better removal efficiency are being developed. However, the removal process can not only be improved by new technologies, but also through optimization of the existing processes.

Alstom Power AB and Linköping University have performed a preliminary study on the need for new sensors in the flue gas cleaning processes at Alstom. It was concluded that SiC based sensors are interesting for the emission control, both in the commercial power plants and also for research and development projects within Alstom. The study has continued as a project, which focuses on the development of the sensing layers and operating modes of SiC Field Effect Transistor (FET) sensors for the detection of SO_2 and H_2S .

In a power plant, as well as in any processes that involve a large quantity of flowing gas, the main issue that hinders the highest pollution removal efficiency is the non-homogeneous gas concentration throughout the duct perimeter area. Various fluid dynamics simulations have been performed to improve the uniformity of the flue gas. However, it is also necessary to check the real conditions experimentally.

Conventional sensors and/or analyzing equipment are usually expensive. As a result, generally not more than one sensor/equipment is installed in one section of the pipeline. A preliminary study on the sensor system suggested that it is necessary to find cheaper sensors to enable the installation of several sensors in one section of the pipeline in order to get information about the varying gas concentration of the flue gas throughout the duct perimeter area. These types of sensors

will also be beneficial for fine tuning of the process during the design and start-up phase of the flue gas cleaning units.

On the other side, SiC-FET sensors have been proven to perform satisfactorily in the industrial environment [1][2]. Previous studies utilized Pt-gate SiC-FET sensors as CO and HC sensors for the control of domestic boilers [1]. Utilization of SiC-FET as NH_3 sensors has also been performed and has shown promising results [3]. A recent study, in collaboration with Tekniska Verken, Linköping, also support this finding [4]. Moreover, the sensitivity of the SiC-FET sensors can be tuned toward certain target gases [5–7]. In this present study, we have explored the capability of SiC-FET as gas sensors for SO_2 and H_2S .

The objective of this study is to develop SiC based FET sensors for SO_2 and H_2S . The study includes sensing measurement in the laboratory and in the desulfurization pilot unit (for SO_2). It also involves a detection mechanism study, which was performed experimentally with DRIFT and mass spectroscopy and theoretically by quantum-chemical calculations. Focus is primarily on SO_2 in this thesis because the process of SO_2 detection is more complex as compared to that of H_2S .

Flue Gas Cleaning Processes and Target Gases

2.1 Flue Gas Cleaning Processes in Thermal Power Plant and Sulphur Dioxide as Target Gas

Despite the current focus on the electricity production from renewable energy resources, thermal power plants still contributes to more than 70% of the total power generation [8]. During the combustion of the fuel in the boiler, some pollutants are produced as by-products. Environmental regulations and demands from the shareholder act as a driving force for the development of the flue gas cleaning technologies.

Depending on the fuel, the major pollutants in the flue gas are usually particulates, sulphur oxides, nitrogen oxides, acid compounds like HCl and HF, heavy

Figure 2.1: Generic air quality control system for thermal power plant [9]

metals, and carbon dioxide. The generic arrangement of a flue gas cleaning system is shown in Fig. 2.1.

Power generation, from large combustion plants, contributes to around a quarter of the total NO_2 emission. The nitrogen oxides is reduced to N_2 and water by a reaction with NH_3 , either at high temperature directly in the flue gas or over a bed of catalyst in the NO_x control unit. The latter process is called SCR, selective catalytic reduction, and is generally more preferred due to the high removal rate and lower temperature requirement. However, the catalyst poses another requirement such as lower particulates and sulfur content in the flue gas.

The most common processes to remove particulates from the flue gas are electrostatic precipitation and bag filter. The particulate removal process is combined with sulfur removal in some desulfurization technologies [9].

The largest CO_2 emitters are the transportation sector and the power generation. Lower emission from power generation in large combustion plant can be achieved by CO_2 capture technology. The most common method for CO_2 removal in industrial applications is absorption with amine solution, for example monoethanolamine (MEA). In this case, the flue gas is led through some absorption column, where it is contacted with the liquid absorbent. Then, the CO_2 rich absorbent is heated for regeneration before recycled back to the column. Some other solution with basic (high pH) nature can also be used as absorbent. Another alternative for capturing the CO_2 is oxy-fuel combustion where pure O_2 is used for the combustion instead of air. The product will mainly consist of CO_2 and water that can be separated easily.

The focus of this study is on the flue gas desulphurization system. Fossil fuels generally contain sulfur compounds. When they are combusted, the sulfur will be oxidized to SO_2 , which is deemed an air pollutant since it is the precursor of acid rain, forms acid particulates, and is dangerous for human health. Therefore, the emission limit for SO_2 is strictly regulated. It is relatively stable in this form and can only be oxidized at relatively high temperature in the presence of a catalyst.

Policy measures for the limitation of sulfur emission have been applied since 1970s for power plant generation application, which is responsible for around 70% of the

SO₂ emission. Sulfur in the form of SO₂ is considered as one of the major concerns in the flue gas purification process. This is because the concentration of SO₂ is quite high compared to other impurities, and the danger it poses to the environment.

Depending on the fuel, the SO₂ concentration is varied from around 500 ppm to several percent at the inlet of the desulfurization units, and around 0 – 50 ppm at the outlet. The flue gas temperature is usually around 200°C at the inlet of the desulfurization unit. Depending on the type of the desulfurization unit, the outlet temperature of the gas can vary between 70 – 150°C. The most common technology for removal of SO₂ is through oxidation and reaction with lime to form gypsum. This reaction can be achieved in several ways. The most common is in the gas-liquid absorbers, where the lime is injected into the unit in the form of slurry. However, more and more advanced and efficient technologies are continuously developed for sulfur removal. Alstom has developed both dry and semi-dry systems, where the lime is injected in the form of powder, and in some cases mixed with ash/dust. In this process, the SO₂ reacts with lime powder and/or absorbs in the dust and form sulfate containing dry rest products

SO₂ sensors are needed to monitor the desulfurization process. Conventionally, some samples are extracted from the process and analyzed in the laboratory. In some other application, an optical gas analyzer is employed for SO₂. However, these methods are either expensive or time consuming. As discussed in chapter 1, it is expected that small and cheap sensors can provide closer monitoring of the process and help improve the uniformity of the flue gas concentration in the flue gas duct, and thus increase the efficiency of the desulfurization system. It should be noted that there are many other gases that might be present in the background, such as O₂, H₂O, HCl, NO_x, and CO₂. The concentrations of these gases vary depending on the processes upstream the desulfurization unit, and this might influence the sensor response.

Moreover, sulfur compounds are known as catalyst poison [10] [11]. Sulfur compounds can attach rather strongly to the catalyst, and therefore, the desorption energy is high, which is a disadvantage for sensors with a catalytic metal gate.

2.2 Flue Gas Cleaning Processes in Geothermal Power Plant and Hydrogen Sulfide as Target Gas

Part of this thesis concerns development of H_2S gas sensors that could be employed in geothermal power plants. Geothermal is one of the renewable energy sources. In geothermal power generation, the heat source is generally steam that is formed deep down in the earth. The steam is extracted to power a steam turbine, and the condensate can be recirculated back to the earth or purged [12].

During the extraction of steam/fluid, it is common that other non-condensable gases are also released. The constituents of the non-condensable gas can vary greatly depending on the reservoir. However, generally it contains H_2 , CO_2 , H_2S , CH_4 , Ar, and N_2 . The concentration of each gas can also vary from ppb level to several hundreds ppm or percent.

H_2S is produced naturally from sulfide hydrolysis or the activity of sulfide microorganisms. It is emitted during the steam extraction in geothermal power generation and also during the anaerobic digestion process in the biogas production. As a pollutant, H_2S is very toxic and flammable. Due to health and environment concerns, it is very important to ensure that H_2S is not released to the atmosphere. Chronic exposure of H_2S may cause nervous system and respiratory disease [13] [14]. The H_2S may also be found in the condensate of the steam turbine. However, this study will only focus on the H_2S in the non-condensable gas phase.

H_2S is removed from the non-condensable gases by oxidation to SO_2 or by absorption with iron based absorber to form FeS_2 . The iron absorber can be in the form of solid scavenger with fixed bed or fluidized bed absorber, or in the liquid form with gas-liquid contactor [H_2S removal]. The background gas temperature is normally around 150°C for the geothermal power plant.

Available Sensor Technologies

There are several considerations in choosing the sensors for a certain application. The most important are the types of target gas, the water vapor content, the operating temperature that must be higher than the temperature of the gas, the dust level, the oxygen content and variation (around 6% in the flue gas), the presence of other gases, and several other factors.

The conventional sensors that are used in power plant applications are usually optical sensors like FTIR (Fourier Transform Infrared Spectroscopy). They are superior for several chemical species measurement in gas because of their high accuracy and sensitivity. However, they are expensive and have disadvantages in the environment where there is vibration, uneven surface, or high dust levels. This chapter covers available sensor technology for SO_2 and H_2S detection in high temperature applications and their detection mechanism.

3.1 Metal Oxide Semiconductor gas sensors

Metal oxide sensors are one of the most common sensors for high temperature detection, especially in a price-sensitive application. The development of the metal oxide sensor began in 1962 [15]. The development was triggered by the law in Japan regarding the requirement of an alarm for households using gas for cooking. The patent was first published by Taguchi [16].

Metal oxide sensors have been developed continuously for decades. There are several commercial sensors available. Figaro [17] developed a series of metal oxide gas sensors for hydrocarbon, hydrogen, and other combustible gases, gaseous pollutants such as CO , NH_3 , NO_x , and H_2S . Their sensors, which typically are

Figure 3.1: Working principle of metal oxide gas sensors

based on SnO_2 are operated at high temperature (around 300°C to 500°C). At this temperature oxygen ions adsorb on the sensor surface, pick up electrons, and thus become negatively charged. Adsorbed oxygen in the grain boundaries creates a potential barrier, which influences the electrical resistance as shown in Fig. 3.1. In the presence of reducing gas, the surface coverage of the adsorbed oxygen ions decreases. This results in a decrease of the resistance, which is measured as sensor response. Besides Figaro, a large number of companies, among them Alpha-MOS [18], Alphasense [19], and Applied Sensor [20], have also developed series of metal oxide gas sensors for various gas detection. However, not many of them are dedicated to SO_2 .

Although not many sensors have been commercialized for SO_2 , continuous development is still performed to enhance the performance of the metal oxide sensor. The most common material for metal oxide gas sensors for both SO_2 and H_2S is based on SnO_2 [21][22][23]. However, studies exist on development of new material such as decorated graphene [24][25], the SCR catalyst [26], or metal (Pt, Pd, Au) decorated WO_3 [27], which has proven to be promising for SO_2 . Both SnO_2 based [23] and Pt decorated WO_3 [28] are examples of metal oxide gas sensors that are developed for H_2S . It is also possible to modify the shape of the sensing layer to enhance the response, such as WO_3 nanoparticles [29] and SnO_2 nanowires [22].

However, since the response is highly dependent on adsorbed oxygen, metal oxide sensors are very sensitive to a change in oxygen concentration in the background. In addition, water and humidity also influence the response of metal oxide sensor significantly. These factors are the main weaknesses in the flue gas cleaning applications.

Figure 3.2: The working principle of YSZ lambda sensors. A potential is measured if the oxygen concentration is different on the upper and lower surface of the sensor [30].

3.2 Electrochemical and Solid Electrolyte gas sensors

3.2.1 Electrochemical gas sensors

Electrochemical cells usually have relatively high selectivity. Commercial SO_2 and H_2S electrochemical sensors are available from Alphasense [19]. However, these sensors can only work in the operating temperature from -30°C to 50°C and low humidity environment, which is not the case in most processes for flue gas cleaning.

3.2.2 Solid Electrolyte gas sensors

Electrochemical cells based on solid electrolytes have been employed for accurate chemical sensing [30]. One of the most mature types of this sensor is the yttria stabilized zirconia (YSZ) based lambda sensor, which is normally used in automotive industry to control the excess air to the engine based on the oxygen concentration. Companies like Bosch and Denso have produced and commercialized lambda sensors.

As illustrated in Fig. 3.2, the lambda sensor work by using catalytic and electrochemical reactions at the electrode surface, which can be modified by an applied potential, temperature, and electrode material. In the YSZ bulk, oxygen vacancies are created by replacing zirconium ions with yttrium. At the surface, Pt is employed as electrode to enhance oxygen decomposition. Formed oxygen ions diffuse via the vacancies through the bulk of the material. The difference between the oxygen concentration at the two surfaces surrounding the bulk is measured as a potential difference [30].

For both SO_2 and H_2S , the development of the solid electrolyte gas sensor is still at an early stage. There is no commercial sensor available yet. However, there are many concepts that have shown promising results. The development started in 1980s [31] by combining the NASICON ($\text{Na}_3\text{Zr}_2\text{Si}_2\text{PO}_{12}$, Na^+ conductor) electrochemical cell with a porous layer of sulfur salt like Na_2SO_4 as auxiliary phase. Utilization of NASICON electrolyte combined with SCR catalyst, with Pt or Au electrode, has also been studied for SO_2 sensing [32]. It is also possible to use the NASICON based sensor for H_2S [33]. Sensors based on YSZ have also been developed, for example combining it with Pt electrode and two different oxides for SO_2 detection at a very high temperature [34] or with a NiMn_2O_4 electrode for detection of low concentrations of H_2S . It has also been shown that a zirconia based sensor with lanthanum sulfate can be employed as SO_2 sensor [35].

Overall, solid electrolyte sensors demonstrate a very good accuracy and low dependency of the oxygen concentration. However, they also have several weaknesses, which were described by Yamazoe et. al. [31]. One of them is the need for very high operating temperature, which might waste energy during the sensor operation. To avoid dependency of the oxygen concentration, an oxygen sensitive half cell is combined with the main oxygenic gas sensitive half cell. In some cases, there might anyhow be some oxygen that interfere with the measurement of an oxygenic gas like SO_2 . It is necessary to incorporate the oxygen sensitive half cell in the characterization of the oxygenic gas sensitive half cell. It is also necessary to study the stability of the interface between the oxygen sensitive cell and the oxygenic gas sensitive cell, since they might react and cause instabilities.

3.3 Fiber optic and other optical Sensor

Besides Fourier Transformed Infrared Spectroscopy (FTIR) that is currently used in the pilot plant by Alstom Power AB [9], there are also several other optical based concepts that have been developed in recent years. The optical sensors has lower price, but also lower accuracy than the high-end laboratory equipment, but still provide better selectivity as compared to semiconductor gas sensors.

Many chemical species have specific absorption pattern when exposed to a certain light source [36]. This pattern can be used to identify the chemical composition.

Several concepts have been studied for the detection of SO_2 both in the visible and UV regions, with the detection limit of 1 ppm [36] [37]. Optical fibers can also be employed as the sensing element for SO_2 and H_2S on top of its use as the communication system [38] [39].

Gas analyzers with optical technologies are fully developed. Commercial sensors based on optical absorption spectroscopy [37] for SO_2 and H_2S are available from major instrumentation companies like Sick or Honeywell. However, they are much more expensive as compared to semiconductor gas sensors. In addition to the price, optical sensors usually have a light source that is not very resistant to vibration, which occur most of the time in the flue gas cleaning process. This will create additional cost to provide a special support for the optical sensor.

3.4 Field Effect Transistor gas sensors

After the invention of Si-FET sensors with Pd gate for H_2 sensing in the mid 1970s [2], continuous development has enhanced the performance of the sensor toward different target gases for industrial applications. From the 1990s, the incorporation of SiC as semiconductor material for the sensors [40] [41] enables the operation at higher temperature (up to 1000°C). The stability, inertness, and high temperature properties of SiC fit the requirement for different high temperature and harsh environments applications, especially automotive and power generation activities [3] [42] [43] [44].

For high temperature application, solid state sensors usually have a superior performance. For solid state sensors in this application, FET sensors have more advantages than metal oxide sensors due to its ability to give satisfactory response in low oxygen level and high humidity atmosphere, which usually is difficult for MOS sensors. As described in previous studies [45] [3], SiC-FET sensors are not very sensitive to a change in humidity. However, they do give a different response between dry and humid gas. The change in response due to humidity normally saturates at a low relative humidity level of around 2%.

Figure 3.3 shows the schematic of a SiC-FET devices. The voltage is applied between source/gate and drain and the current flows through the channel. The gas decomposes on the catalytic metal gate and interacts with the oxide/insulator due

Figure 3.3: Schematic cross-section of SiC- FET device [Reproduced from Ref. 44 with permission from Elsevier]

to the (reversible) diffusion of gas species from the metal to the insulator surface. The interaction creates a polarized layer that changes the electric field between the gate and the semiconductor, resulting in a change in the conductivity of the channel [43] [46].

Several studies have been performed regarding the investigation of the influence of the morphology of the sensing layer to the sensing characteristics [47] [48]. The studies describe that depending on the gate material, thickness, and porosity, there are different sensing mechanisms involved, especially between dense and porous sensing layers that change the reaction on the sensor surface. For the ammonia case, it is obvious that thin and porous metals lead to higher reactivity. Based on those studies, the sensing principle of the porous SiC-FET devices is built as shown in Fig. 3.4

In the case of hydrogen containing compounds, for which hydrogen dissociate during adsorption on the surface, it is illustrated that the decomposed H ions diffuse along the surface of the metal. The hydrogen adsorbed at the boundaries between gas-metal-insulator may diffuse further on the insulator surface to create a polarized layer of OH groups with the oxygen in the insulator. The result of these phenomena is an electric field in the oxide, which changes the mobile carrier charge/concentration in the channel, which is indicated by a change in the $I - V$ characteristics of the devices. The detection mechanism for non-hydrogen containing gases is reported in other studies supported by DRIFT spectroscopy [49] [50]. This is complicated and to some extent understood for CO, but no other non-

Figure 3.4: SiC-FET Sensing Principle [Reproduced from Ref. 43 with permission from Springer]

hydrogen containing gases. More DRIFT spectroscopy, mass spectrometry studies of reaction products and theoretical modeling may reveal more about this in the future.

The studies on SO₂ oxidation on the Pt catalyst system have been reported before for two cases; stand alone Pt surface [51] or with different oxides [52] [53] [54]. Lin et. al. [51] found that while oxygen prefer the bridge adsorption site, SO₂ and SO₃ prefer a-top adsorption site. Based on the calculation, the reaction between pre-adsorbed SO₂ and pre-adsorbed O₂ requires higher activation energy compared to the reaction of pre-adsorbed O₂ directly with SO₂ in the gas phase. Overall, the mechanism of sulfur oxidation is very sensitive to the environmental condition, especially the oxygen coverage on the Pt surface [51]. When different oxides were studied [53], it was observed that SiO₂ did not adsorb SO₂ as effective as more basic oxides, such as Al₂O₃ or MgO. This observation was confirmed by another study that shows that without the presence of Pt, the affinity of SO₂ to SiO₂ is very low [11]. This is good for the sensor performance as this gives the possibility for the sensor to recover after SO₂ exposure. Xue et al [53] also found that the SO₂ oxidation rate is highest at about 350 – 400°C, for different Pt coverage in SiO₂. The reaction rate becomes more sensitive to the Pt coverage at a lower reaction temperature.

For H₂S, it is suspected that the response comes from the hydrogen ions as is the case for hydrogen. Although it is also possible to have a response from removal of the oxygen layer on the sensor surface, it seems that the formation of the hydrogen polarized layer might give stronger influence.

Figure 3.5: SiC-FET Sensing Principle - Response at different temperature for Pt and Ir-gate sensors [Reproduced from Ref. 43 with permission from Springer]

Selectivity of the SiC-FET can be tuned toward certain target gases by changing the catalytic gate material [55] [56] [6] [49] and/or the oxide material [57] [58], depending on the reactivity of the material to the target gases. Besides the material, it is also possible to adjust the sensitivity and selectivity of the sensors by changing the operation temperature and or method of operation as described in the subsections below.

3.4.1 Operating temperatures

The sensing mechanism in SiC-FET sensors depends on the adsorption of the molecules, decomposition, and reaction on the catalytic metal, product formation, and desorption of the reaction products from the sensor surface. Therefore, the sensitivity and the selectivity of the sensors are very temperature dependent. Previous studies have shown that different gases have different optimum sensing temperature for different catalytic metal gate as shown in the Fig. 3.5 for Pt-gate and Ir-gate SiC-FET gas sensors [55].

Ideally, to achieve good selectivity, the sensor should be operated at a temperature where the response to the target gas is high in contrast to low response from the other gases in the background. However, this is not always possible. For most industrial applications, the concentration of some other gases in the background might change at some point resulting in a higher change in the sensor response to this particular gas as compared to the target gas. This problem leads to further research in the field of sensor operation and data analysis to achieve better selectivity, such as by installing sensor arrays or the use of temperature or bias cycling as further discussed in the next chapter.

3.4.2 Gate and substrate bias

Nakagomi et al [59] found that applying a substrate bias can amplify the sensitivity of MISFET (Metal-Insulator-Semiconductor FET) sensors for H_2 and provide the possibility to control the base line. Subsequently, the same group studied the gate bias influence on the sensing behavior [60]. This possibility to manipulate the sensing behavior is very interesting and further exploration, performed with CO as the target gas, shows consistent results [61]. These studies combined with smart operation led to the possibility of exploiting gate bias cycling to improve the selectivity of MISFET sensors to different target gases as indicated in the recent study [62]. The results show the potential of the method to improve sensor selectivity.

Dynamic Operation, Signal Processing, and Multivariate Data Analysis

4.1 Temperature cycled operation

As previously mentioned, the sensing behavior is temperature dependent. The response evolution due to the change in the operating temperature is also different from one gas to the other, which creates a special signature for each gas. Using multivariate data analysis [63] to interpret the sensor signal, it is possible to consider not only the maximum response of the sensor, but also the slope of the response/recovery or other desired features in the signal processing and data analysis. The more features extracted from the dynamic response, the better differentiation can be achieved from the measurements.

This method can be performed by operating one sensor at different temperatures in cyclic fashion [64]. Temperature cycling gives the benefit of operation with sensor arrays without having the drawbacks that come with it. In sensor array operation, it is difficult to ensure that all sensors work as per the condition in the calibration after a certain time of operation. If one of the sensors fails, the whole system will suffer. This problem does not exist in the temperature cycling operation using only one sensor [64]. Depending on the response time and stabilization time of the sensor during change of the operation temperature, one cycle is usually below 1 minute, which is almost the same time needed by the optical reference instrument. With the correct setting and data training, this method is a very promising option for improving the selectivity of FET sensors.

Figure 4.1: Result from Temperature Cycling Methods for NO_x Detection. Figure to the left shows the temperature cycle with indication of the gas molecules, which are expected to influence the sensor signal at the different chosen temperatures and the sensor signal in nitrogen. Figure to the right shows the data evaluation by LDA. [Reproduced from Ref. 67 with permission from Springer]

This method has been proven successful to identify certain target gases with changing background gases and for the influence of changing humidity [65] [66]. It was possible to identify not only different types of gases, but also the concentration evolution in one target gas. A recent study on quantification of NO_x with MISFET sensors [67] [68] showed the capability of this method to measure the NO_x in a changing background gas mixture despite the small response of NO_x in static sensor operation, as shown in Fig. 4.1.

4.2 Signal Pre-processing

Smoothing of the data is necessary to remove the noise from the raw sensor signal. The smoothing is performed with Savitzky-Golay convolution filter [69]. This method is chosen because the act of fitting the adjacent data with the low polynomial can smooth the data without distorting it.

If the sensor experience drift in an operation with extended period, normalization can be employed to minimize the influence of the drift. The normalization can be performed by dividing the data with the mean value or by subtracting it.

The next step is collecting the features to be used for the multivariate data analysis [63] such as mean value, slope, standard deviation, and norm from the different intervals in the temperature cycle operation.

4.3 Multivariate Data Analysis

Controlled multivariate data analysis [63] needs to be performed to enable the quantification of the test gas. In this study, Linear Discriminant Analysis (LDA) [70] [71] [72] and Partial Least Square (PLS) regression [73] [74] is employed to evaluate the data. Both methods try to maximize the co-variance between groups and minimize the co-variance within the group. For data points in a space with a large number of dimensions (here, each evaluated point in the temperature cycle become one dimension), the number of dimensions can be reduced to two by introducing a new axis, which should represent as much of the variance in the data as possible, but still in agreement with the control values that were used for calibration. The second axis should be added perpendicular to the first, and constructed based on the same principle as the first axis, which based on the largest variation in the data that is still in agreement with the control values in the calibration. In this way, known sensor signal versus concentration data points are used for calibration and to build a model, by which, if successful, it is possible to determine the concentration of other unknown data points.

In some cases, for example where there is a change in the background gas that interfere strongly with the sensor signal, it is necessary to perform 2-step multivariate data analysis. The first step is performed to identify the background gas, and the second step is for the quantification of the target gas. This method was first introduced for metal oxide sensors [75] [64]. However, a previous study has proved that the same concept can be applied to SiC-FET sensors [68]. This method certainly improves the accuracy of the gas detection by incorporating the influence of the background into the data evaluation.

Sensor Fabrication and Sensing Measurement

5.1 Sensor Fabrication

5.1.1 Deposition of the sensing layer

The sensing layer (denoted catalytic gate in Fig. 3.3 and Pt/Ir in Fig. 3.4) was deposited by direct current (DC) magnetron sputtering.

Magnetron sputtering is one of the physical vapor deposition methods. It utilizes ionized gas to eject particles from a target and deposit the particles as a thin film on a dedicated substrate [76]. The magnetron confines the plasma on the target, resulting in a higher deposition rate. The system is described in a schematic diagram in Fig. 5.1.

A porous film creates three phase boundaries between the test gas, the catalytic

Figure 5.1: Schematic diagram of the DC magnetron sputtering system

Metal	Thickness (nm)	Current (mA)	Voltage (V)	Deposition Pressure (mTorr)
Pt	20-30	400	480	50
Ir	20-30	400	400	50

Table 5.1: Deposition Parameter

Figure 5.2: SEM picture of the catalytic metal gate

metal, and the oxide support. This type of film is produced through deposition at a relatively high pressure. The deposition parameters for the sensing layers are listed in Table 5.1.

5.1.2 Morphology characterization of the sensing layer

Scanning electron microscope (SEM) is a high resolution microscope that uses high energy electrons instead of light to create images. It works by shooting an electron beam on the sample and detect the resulting signal (backscattered and secondary electrons) from the electron-sample interaction, from which the images are formed. The electron beam is produced by the electron gun. The path of the electron is held vertical within a vacuum chamber [77] [78].

This method is utilized to characterize the morphology of the sensing layer, especially the porosity of the sensing layer. Figure 5.2 shows the SEM image of the Pt and Ir gate of SiC-FET sensors.

5.1.3 Sensor assembly

After the deposition is completed, the metal at the unwanted area is removed normally by the lift-off method (the sensor surface was previously patterned using

Figure 5.3: Sensor assembly

a resist layer). The sensor chips are cut from the wafer and mounted on the 16 – *pin* header as shown in Fig. 5.3. The headers are utilized as the platform to connect the sensors to the control board. The heaters and Pt100 are welded to the 16 – *pin* header. The sensor chips are glued to the heater, and the source, drain, and gate of the sensors are bonded with gold wire to the header. The heater and the Pt100 temperature sensor are connected to the PID controller to provide accurate individual temperature adjustment of the sensors. The electrical board provides constant current as the input to the sensor and the drain-source voltage is taken as the output of the sensor and transmitted to the data acquisition system.

5.2 Performance Testing

5.2.1 Laboratory measurement

The current flow through the device is kept constant in these sets of experiment as shown in Fig. 5.4. The resulting drain voltage is then measured continuously and recorded in the Data Acquisition System.

The gas mixing system consists of a series of flow controller as described in Fig. 5.4. The gas flow was adjusted by the gas mixing program connected to the system. The concentration of the test gas is adjusted by tuning the flow of the necessary gases. The test gas is introduced to the sensor chamber in the form of gas pulses in order to also study the recovery between different concentrations of gas. During recovery, the test gas is stopped, whereas the carrier gas continuously flows, and the total flow is always kept constant.

Figure 5.4: Measurement assembly

5.2.2 Pilot Unit Measurement

It is difficult to achieve a condition close to the real application in the laboratory setting, since the gas flow is much smaller, the gas piping system is not as large and the concentration of the SO_2 does not vary as fast as in the real application. However, it is also difficult to do real performance testing in power plants due to for example the dust content in the gas, and installation difficulties due to the inflexibility of the normal operation. To achieve something in between, a condition that is close enough to the real application and also controllable, the sensor was installed at the outlet of an operating desulfurization pilot unit.

As shown in Fig. 5.5, the desulfurization unit removed SO_2 from the flue gas by mixing a certain amount of lime ($CaOH_2$) and dust with the gas [20]. The SO_2 reacted with lime and formed dry rest products. The dust mixture was separated from the gas with a fabric filter. The dust was collected in the bottom area of the filter and recycled into untreated gas. The clean gas is vented through the outlet of the pilot unit, where the SO_2 concentration and the gas temperature were measured. New reactant, such as lime, was added to the dust mixture if the SO_2 concentration in the outlet became too high. Water could be added to the system if the temperature was too high, due to the exothermal nature of the SO_2 absorption.

Figure 5.5: Dry desulfurization pilot unit. The sensors are located at the outlet of the system as indicated in the drawing [Re-drawn from Ref. 9]

Flue gas was simulated in the desulphurization unit by burning propane and then adding the pollutants under study, such as SO_2 and HCl , into the gas mixture. At the outlet of the unit, the O_2 , CO_2 , and H_2O concentrations, and also the temperature varied depending on the propane combustion and other processes in the desulphurization unit. The SO_2 and HCl concentrations varied based on the injection of SO_2 and HCl at the inlet, and also the subsequent absorption process.

The overall variation is listed below:

SO_2 : 0 – 4000ppm

O_2 : 0 – 22%

CO_2 : 0 – 7%

$\text{H}_2\text{O}(\text{absolute})$: 0 – 20%

HCl : 0 – 300ppm

Gas temperatures : 60 – 150°C

The SiC-FET sensors were installed at the outlet of a desulphurization pilot unit, as shown in Fig. 5.5. Each sensor was installed in a sensor holder with thread connection and then inserted into the flue gas duct.

The pilot was run continuously for $4 \times 24h$. However the data presented in this study only covered 45 hours of measurement due to technical difficulties during the set-up of the equipment.

Detection Mechanism Studies

Experiment with mass spectroscopy, complemented with quantum chemical calculations were performed to study the mechanism of the SO_2 and H_2S detection with SiC-FET sensors. Due to the more complicated phenomena for SO_2 detection, DRIFT spectroscopy was also performed on Pt/ SiO_2 model surface.

6.1 Experimental Methods

6.1.1 DRIFT spectroscopy

DRIFT spectroscopy is one of the methods for the study of the reaction and detection mechanism on the sensor surface in order to reveal details in the detection mechanism. It is performed by focusing IR light to the sample, which in this study is in a powdered form, and measure the resulting scattered light [79]. This method enables the observation of the adsorbed and formed species on the sample surface. It is possible to distinguish between adsorbates on the metal, on the insulator, or in the gas phase.

One of the difficulties we find is that the sensor does not have enough surface area to be measured with this method. Based on the previous studies [49] [50] [80], it is possible to model the sensor surface by silica powder, which acts as the oxide support, impregnated with the catalytic metal.

Another challenge encountered during the experiment is that the wavelength for adsorbed sulfate, which most likely will be the product of the surface reactions of the sulfur compounds with adsorbed oxygen, is in the wavenumber region where there is a strong IR radiation. It was discovered that diluting the sample decreases

the effect. Diamond dust was chosen over KBr, the standard compound for sample dilution, due to the inertness of the diamond to sulfate exposure.

6.1.2 Mass spectroscopy

A mass spectrometer is attached at the downstream of the sensor and the DRIFT spectroscopy system to detect the residual gas. Observation of the residual gas gives more insight of the product of the reaction and accumulation of molecules on the sensor surface. The resulting data from this measurement can be compared with the data from DRIFT spectroscopy to build a model of the surface reactions and thereby suggest the detection mechanism, which creates the sensor response.

The gas flows through a capillary to the interior of the mass spectrometer, where the gas is ionized. Then, it is accelerated and deflected by a magnetic field. The deflection depends on the charge and mass of the ions. The more charge the ion has or the lighter they are, the more deflection is achieved. The last part of the system is the detector. The gas molecules might be fragmented and form smaller ions during the process. The calculation of the fragmented part is very important for the quantitative analysis. All of these processes have to be performed under vacuum condition inside the spectrometer to enable the detection of reactive and short-lived ions.

6.2 Theoretical Calculations

Besides the experimental work, the interaction between the molecules and the catalytic metal or the gate oxide has also been studied by quantum-chemical calculations as discussed in this chapter.

6.2.1 Quantum-chemical computations

Quantum chemistry is based on the solution of the Schrödinger equation [81], for electrons and nuclei. The Schrödinger equation depicts the relationship between the wave function (ψ), the energy (E), and the Hamiltonian operator (H). The Hamiltonian operator (H) includes the kinetic energy, the operators of the elec-

trons, and the potential energy operators of the the electron-nuclei, nuclei-nuclei, and the electron-electron interaction, as well as the interaction with the external potential. For multi-electron atoms, it is impossible to obtain an analytical solution of the Schrödinger equation. However, it is still possible to solve it numerically [81].

One approach to solve the Schrödinger equation for molecular system is first principles *ab initio* calculations [82] [83]. This kind of calculation is performed without any aid of empirical data. The simplest common type of *ab initio* calculations is the Hartree-Fock (HF) method [82]. In the HF, each electron is described by a one-electron wave function and the electron-electron interaction is approximated by a mean field, which allows for a set of one-electron equations to be solved.

Density Functional Theory (DFT) [84] is a more recent type of method. It has many similarities with the HF method. However, among other things, it includes an additional term that accounts for the correlated motions of electrons. This gives the advantage of more accurate results in most cases [82]. Hybrid functionals [82] combine *HF* exact exchange and DFT exchange correlation functionals. Much effort has been put into formulation of hybrid functionals that can be utilized for different systems. *B3LYP* [85] [86], which is used in the present study, is one of the most widely used hybrid functionals.

All calculations in this study were performed with the *Gaussian03* program [87].

6.2.2 Clusters and surface models

In the computational modeling, the catalytic metal gate on the sensor was represented by clusters of metal atoms. Several metal clusters were studied with different number of atoms and spin multiplicities.

The clusters were built by constructing a large cluster with atomic position as in the crystal structure of the respective metals as listed in Table 6.1. Then smaller clusters with the desired numbers of atoms were cut out from the large cluster. These cluster structures were the starting point for geometry optimizations, in which the atomic positions were allowed to relax in order to find energy-minimum structures.

Parameter	Pt	Ir
Space group	Fm3m (225)	Fm3m (225)
Structure	cubic close-packed	cubic close-packed
a (pm)	392,42	383,9
Number of electrons	78	77

Table 6.1: Crystallographic data for the Pt and Ir crystal structures

$$\Delta E = \frac{E_{cluster} - nE_{atom}}{n} \quad (6.2.1)$$

Cohesive energies were calculated for the geometry-optimized clusters. Cohesive energy (ΔE) is defined in 6.2.1, where n is the number of metal atoms in the cluster. The structures of some of the geometry-optimized Pt and Ir clusters are shown in Fig. 6.1.

Larger clusters constitute more realistic models of the sensor gate. However, smaller clusters require less computational time. Still, one needs to ensure that the small cluster contains a sufficient number of atoms to represent the surface where the reaction is carried out.

Besides the conveniently small clusters, larger clusters were also employed to simulate the sensor surface. As shown in Fig. 6.2, a 22-atom cluster was used to model the Pt(111) surface and a $\text{Si}_{10}\text{O}_{12}(\text{OH})_{16}$, cut from the β Cristobalite crystal structure, was used to model the SiO_2 surface.

6.2.3 Reaction mechanism energy profile

In this modeling study, we focused on investigating some key reaction steps in the reaction mechanisms of gas molecules on the sensor surface. Adsorption energy is the energy difference between the adsorbed reactants and the sum of the energies of the isolated substrate and the reactant molecules. The same applies for desorption energy, i.e. it is calculated from the energy difference between the product molecules adsorbed on the metal surface and isolated substrate and the product molecules.

Number of atoms	Pt	Ir
4
5
10
13
17
20

Figure 6.1: Optimized geometries of different Pt and Ir clusters

Figure 6.2: Optimized geometries of $\text{Si}_{10}\text{O}_{12}(\text{OH})_{16}$ and Pt_{22}

The transition states, which correspond to saddle points on the potential energy surface, need to be localized first in order to compute the activation energy. Once the transition state is found, the activation energy is calculated as the difference between energy of the adsorbed transition state structure and the sum of the energies of the individual adsorbed reactants.

The varieties in adsorption/desorption energies and in activation energies for different reactions on different metal surfaces were used to rationalize different observed sensor responses.

6.2.4 Vibrational spectra calculations

Vibrational frequencies were computed from a normal-mode analysis based on the analytical second derivatives of the energies with respect to nuclear displacement [87]. By combining the vibrational frequencies with computed intensities from the derivatives of the dipole moment, the infrared (IR) vibrational spectra were obtained. In the present study, comparison between observed and computed vibrational spectra were used to identify species on the silica surface.

Summary of the Results

7.1 Performance of field effect transistor as sulfur dioxide sensor in thermal power plant application (Paper 1 and 2)

Sulfur dioxide is a very difficult gas molecule for SiC – FET sensors due to its stability and strong bonding in the sulfate form. Different gate materials (Pt, Au, Ir) have been tested. However, with static operation, the response was small and saturated at a low level of SO₂ concentration, even at the optimum operating temperature. Static operation provided the possibility to identify the presence of SO₂ but not to quantify it. Dynamic operation with temperature cycled operation (TCO) and multivariate data analysis was performed to improve the sensor performance. The TCO enabled the measurement of SO₂ at different operating temperatures in a cyclic fashion. Several features from different intervals were taken to feed the multivariate data analysis after the data pre-processing. It was possible to perform SO₂ quantification with Linear Discriminant Analysis (LDA). However, the accuracy in the evaluation decreased whenever there was a change in the background gas concentration. To improve the accuracy of the sensor in a changing background, 2-step LDA was performed. This method used the first LDA to identify the background gas and the second LDA for the quantification of the SO₂ within a certain background. This method showed promising results in the laboratory and provided a fairly good fit to the SO₂ measurement with SiC – FET sensors when compared to the FTIR reference instrument in the dry desulfurization pilot unit at the Alstom facilities.

7.2 Detection mechanism studies of sulfur dioxide on $Pt - SiO_2$ system (Paper 3 and 4)

In addition to the sensing measurement, studies on SO_2 interaction with the $Pt - SiO_2$ system was also performed experimentally by DRIFT (Diffuse Reflectance Infrared Fourier Transform) spectroscopy and mass spectroscopy of gas downstream of the sensor, and theoretically by quantum-chemical calculations. The first study was the vibrational analysis of the IR spectra both with DRIFT spectroscopy and quantum chemical calculations. It was found that during the exposure to SO_2 , a peak representing surface sulfate appeared, accompanied by negative peak in the region of terminal silanols. The same peaks were also observed in the calculation. The results suggest that there is a formation of surface sulfate due to the reaction of sulfur containing gas with the silanols group on the silica surface. It was difficult to remove this peaks in the oxidative or neutral environment up to 400 °C. This was also the case in the pilot measurement, where the recovery was difficult and sensor surface became saturated after a certain time. Mass spectroscopy measurement indicated that there is SO_3 production in the residual gas when oxygen is present in the gas feed. Previous studies show that without the presence of Pt, silica has low affinity to SO_2 . This confirmed our findings that SO_2 underwent an oxidation process on the Pt surface and both SO_2 and SO_3 can be adsorbed on the silica surface. This process influences the coverage of the surface oxygen and the hydroxyl group on the silica surface, which might influence the sensor signal.

7.3 Hydrogen sulfide sensor in geothermal power generation application (Paper 5)

Pt and Ir sensors were tested against H_2S both in the dry and humid environment. It was found that in the dry environment, Ir sensors show a very large response towards H_2S . Unfortunately this large response was also accompanied by long recovery time. The experiment was continued in humid conditions to simulate the environment in the geothermal application. In humid conditions the sensitivity decreased significantly, especially in the absence of oxygen. It was also observed that there was cross-sensitivity in the presence of light hydrocarbon, such as propene. Performing the sensing measurement in dynamic operation might be an option to explore in the future to improve the selectivity.

Contributions to the Field and Outlook

Using SiC-FET as SO₂ sensors is a new concept which has never been tested before. The main challenge is because the sulfur compound is known as a catalyst poison. However, in this study I applied a known method of temperature-cycled-operation, and developed it to increase the selectivity and sensitivity of the sensor towards SO₂, even when there is a change in the concentration of the background gas. I have also demonstrated the possibility to use this operation method and the limitations of the method both in the laboratory and in the flue gas desulfurization pilot unit. A new design for temperature cycle operation has been developed to improve the accuracy of SO₂ sensing even more. The next step is to add a short period of temperature high enough for sulfate desorption, in the presence of water vapor, in the temperature cycle operation. Additionally, more pilot measurements are necessary in the future to create more relevant data in order to build algorithms such that the sensor signal will represent the SO₂ concentration in the flue gas.

I have also studied the detection mechanism of SO₂ on the SiC – FET. In this study, I have built on the knowledge about the interaction between SO₂ and Pt / SiO₂ system. The implication of this study is the confirmation on the optimum temperature of the sensor and that it is difficult to completely remove the surface sulfate in the oxidative environment up to 400 °C. However, it was mentioned in the previous study with other oxides, that the presence of water vapor will reduce the temperature of sulfate reduction [11, 54, 88]. A study to find the minimum temperature for sulfate removal from the sensor surface in the presence of humidity should be performed in the future to complete the detection mechanism study.

I have also demonstrated for the first time that Ir gate sensors give a very high response towards H_2S , although with the cost of high recovery time, for dry condition in the presence of oxygen. I have also shown that SiC – FET sensors could still detect H_2S in the presence of humidity and absence of oxygen, even though the sensitivity became much smaller. Further investigation is needed to improve the selectivity of Ir-gate sensors in humid conditions and oxygen deficient environments to be able to use the sensor for geothermal applications.

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