MEMS-based electrochemical gas sensors and wafer-level methods

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Front cover images:

The front cover image on the left shows the photograph of the amperometric gas sensor. Top right TEM image shows the horizontal cross-section of the nanoporous membrane, each nanopore is approximately 40 nm in diameter, and the bottom right image shows the sensor packaged with a custom made chip holder.
Abstract

This thesis describes novel microelectromechanical system (MEMS) based electrochemical gas sensors and methods of fabrication.

This thesis presents the research in two parts. In the first part, a method to handle a thin silicon wafer using an electrochemically active adhesive is described. Handling of a thin silicon wafer is an important issue in 3D-IC manufacturing where through silicon vias (TSVs) is an enabling technology. Thin silicon wafers are flexible and fragile, therefore difficult to handle. In addressing the need for a reliable solution, a method based on an electrochemically active adhesive was developed. In this method, an electrochemically active adhesive was diluted and spin coated on a 100 mm diameter silicon wafer (carrier wafer) on which another silicon wafer (device wafer) was bonded. Device wafer was subjected to post processing fabrication technique such as wafer thinning. Successful debonding of the device wafer was achieved by applying a voltage between the two wafers. In another part of the research, a fabrication process for developing a functional nanoporous material using atomic layer deposition is presented. In order to realize a nanoporous electrode, a nanoporous anodized aluminum oxide (AAO) substrate was used, which was functionalized with very thin layers (~10 nm) of platinum (Pt) and aluminum oxide (Al₂O₃) using atomic layer deposition. Nanoporous material when used as an electrode delivers high sensitivity due to the inherent high surface area and is potentially applicable in fuel cells and in electrochemical sensing.

The second part of the thesis addresses the need for a high performance gas sensor that is applicable for asthma monitoring. Asthma is a disease related to the inflammation in the airways of the lungs and is characterized by the presence of nitric oxide gas in the exhaled breath. The gas concentration of above approximately 50 parts-per-billion indicates a likely presence of asthma. A MEMS based electrochemical gas sensor was successfully designed and developed to meet the stringent requirements needed for asthma detection. Furthermore, to enable a hand held asthma measuring instrument, a miniaturized sensor with integrated electrodes and liquid electrolyte was developed. The electrodes were assembled at a wafer-level to demonstrate the feasibility towards a high volume fabrication of the gas sensors. In addition, the designed amperometric gas sensor was successfully tested for hydrogen sulphide concentration, which is a bio marker for bad breath.

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To my Parents
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<th>Full Form</th>
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<tbody>
<tr>
<td>3-D</td>
<td>Three Dimension</td>
</tr>
<tr>
<td>CMOS</td>
<td>Complementary metal oxide semiconductor</td>
</tr>
<tr>
<td>WE</td>
<td>Working electrode</td>
</tr>
<tr>
<td>RE</td>
<td>Reference electrode</td>
</tr>
<tr>
<td>CE</td>
<td>Counter electrode</td>
</tr>
<tr>
<td>ALD</td>
<td>Atomic layer deposition</td>
</tr>
<tr>
<td>PCB</td>
<td>Printed circuit board</td>
</tr>
<tr>
<td>ppb</td>
<td>Parts-per-billion</td>
</tr>
<tr>
<td>mlps</td>
<td>mili liter per second</td>
</tr>
<tr>
<td>PEALD</td>
<td>Plasma enhanced ALD</td>
</tr>
<tr>
<td>IC</td>
<td>Integrated circuit</td>
</tr>
<tr>
<td>DRIE</td>
<td>Deep reactive ion etching</td>
</tr>
<tr>
<td>MEMS</td>
<td>Microelectromechanical system</td>
</tr>
<tr>
<td>Rf-MEMS</td>
<td>Radio frequency MEMS</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscope</td>
</tr>
<tr>
<td>TSV</td>
<td>Through silicon via</td>
</tr>
<tr>
<td>SOI</td>
<td>Silicon on insulator</td>
</tr>
<tr>
<td>FET</td>
<td>Field Effect Transistor</td>
</tr>
<tr>
<td>FPGA</td>
<td>Field programmable gate array</td>
</tr>
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</table>

## Chemical Formulas

<table>
<thead>
<tr>
<th>Chemical Formula</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaOH</td>
<td>Sodium hydroxide</td>
</tr>
<tr>
<td>CsOH</td>
<td>Cesium hydroxide</td>
</tr>
<tr>
<td>LiOH</td>
<td>Lithium hydroxide</td>
</tr>
<tr>
<td>HF</td>
<td>Hydrogen fluoride</td>
</tr>
<tr>
<td>HCl</td>
<td>Hydrochloric acid</td>
</tr>
<tr>
<td>KOH</td>
<td>Potassium hydroxide</td>
</tr>
</tbody>
</table>
HNO₃  Nitric acid
LiCl  Lithium chloride
LiBr  Lithium bromide
NaHCO₃  Sodium bicarbonate
DMSO  Dimethly sulphoxide
DMF  Dimethlyformide
THF  Tetrahydrofuran
PEO•LiX  Lithium salt in a polymer matrix
PVA/H₃PO₄  Polyvinylalcohol/phosphoric acid
ZrO₂  Zirconium oxide
NO  Nitric oxide
H₂S  Hydrogen sulphide
CO  Carbon monoxide
O₂  Oxygen
CPT  Cyclopentanone
H₂SO₄  Sulphuric acid
NH₃  Ammonia
Bmim NTf₂  1-Butyl-3-methylimidazolium bis(trifluoromethanesulfonylimide
Emim NTf₂  1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonylimide
MeCpPtMe₃  methylcyclopentadienyl- trimethyl platinum
TMA  Trimethylaluminum
List of Publications

The presented thesis is based on the following international reviewed journals:

A. “Temporary wafer bonding and debonding for 3D integration using an electrochemically active polymer adhesive”,
   **H. K. Gatty**, S. Schröder, F. Niklaus, N. Roxhed and G. Stemme

B. “Pt–Al₂O₃ dual layer atomic layer deposition coating in high aspect ratio nanopores”,
   **G. Pardon, H. K. Gatty**, G. Stemme, W. van der Wijngaart and N. Roxhed

C. “An amperometric nitric oxide sensor with fast response and ppb- level concentration detection relevant to asthma monitoring”,
   **H. K. Gatty**, S. Leijonmarck, M. Antelius, G. Stemme and N. Roxhed

D. “A wafer level liquid cavity integrated amperometric gas sensor with ppb level nitric oxide gas sensitivity”,
   **H. K. Gatty**, G. Stemme and N. Roxhed
   Accepted to *Journal of Micromachines and Microengineering*, 2015

E. “An amperometric hydrogen sulphide sensor applicable for bad breath monitoring”,
   **H. K. Gatty**, G. Stemme and N. Roxhed
   Manuscript, 2015
The contributions of Hithesh K Gatty to the different publications:

A. Major part of design, all fabrication, Major part of experiments and major part of writing

B. Major part of design, major part of fabrication, major part of experiments and part of writing

C. Major part of design, all fabrication, all experiments and major part of writing

D. Major part of design, all fabrication, all experiments and major part of writing

E. Major part of design, all fabrication, all experiments and major part of writing
The work has also been presented at the following international reviewed conferences:

A. “A ppb level, miniaturized fast response amperometric nitric oxide sensor for asthma diagnostics”,
   **H. K. Gatty**, S. Leijonmarck, M. Antelius, G. Stemme, and N. Roxhed
   *Proceedings of the IEEE 26th Int.Conf. on Micro Electro Mechanical Systems (MEMS)*, Taipei, Taiwan, pp. 381-384, Jan 2013.

B. “Temporary wafer bonding and debonding by an electrochemically active polymer adhesive for 3D integration”,
   **H. K. Gatty**, F. Niklaus, G. Stemme, and N. Roxhed
   *Proceedings of the IEEE 26th Int.Conf. on Micro Electro Mechanical Systems (MEMS)*, Taipei, Taiwan, pp. 381-384, Jan 2013.

C. “Temporary wafer bonding of thin wafers by electrochemically active polymer”,
   **H. K. Gatty**, F. Niklaus, G. Stemme, and N. Roxhed
   *Proceedings of the Int.Conf. on Wafer Bonding for Microsystems 3D-and Wafer Level Integration*, Stockholm, Sweden, pp. 143-144, Dec 2013 (Oral Presentation)

The work has also been presented at the following workshop:

D. “A ppb-level miniaturized amperometric nitric oxide sensor”
   **H. K. Gatty**, S. Leijonmarck, M. Antelius, G. Stemme, and N. Roxhed
   Medicinteknikdagarna, Stockholm, Sweden, Oct 2013

P.S: Integrated nitric oxide (NO) sensor design (paper D) also appeared in the article titled “MEMS är mums för hälsan” (MEMS are good for your health) under the theme : Medicinteknik published in the newspaper *Electroniktidningen*, Dated April 2014, written by Anna Wennberg.
Chapter 1

Introduction

1.1 Microelectromechanical systems (MEMS)

Today, a mobile phone contains more than ten microelectromechanical system (MEMS) based devices. The number of mobile phones is predicted to increase to approximately two billion by 2020, which would escalate the demand for MEMS devices. The advantage of MEMS devices is their ability to perform complex functions given their small size. MEMS devices are often used in applications such as navigation, image processing and sound processing that are required in mobile phones.

MEMS devices can generally be classified into three categories: sensors, actuators and functional structures. Devices that transduce force, temperature, pressure or any other change in the environment into electrical signals can be classified as sensors whereas actuators essentially convert electrical signals to mechanical motion, heat, or any other form of energy. MEMS based structures are functional elements typically used to assist a device for example microchannels in a micropump, nanoporous structures for high surface area devices, microneedles for drug delivery devices etc. There are typically five main processes that involve the development of MEMS based devices. They are bulk micromachining, surface micromachining, high aspect ratio (HAR) micromachining, wafer bonding and packaging.
The application of MEMS process can be tracked back to the fabrication of a suspended beam structure as a gate electrode in a resonant gate transistor device, by Nathanson et al. in the late 60’s [1]. However, it is only in the early 80’s that MEMS technology started to gain importance with devices such as flow sensors [2, 3], pressure sensor [4], resonator [5] etc. MEMS based actuators such as micromirrors emerged some years later [6]. Recently, functional microstructures have gained importance with devices such as microneedles for painless drug delivery [7] and as microchannels for Lab-on-Chip applications [8]. The success of MEMS technology has given rise to several new interdisciplinary fields such as bio-MEMS [9], optical MEMS [10, 11], microfluidics [8, 12, 13] and RF MEMS [14, 15].

In the future, a comprehensive measurement system such as a personalized health monitoring system using mobile phones could be envisioned in which MEMS devices are likely to play a key role. This calls for the development of novel MEMS based devices in the field of medical systems such as electrochemical sensors, glucose level sensors, heart rate monitor etc. MEMS based electrochemical sensors can provide the paradigm shift necessary for the development of medical sensor systems.

1.2 MEMS based electrochemical sensor

Electrochemical sensors essentially generate electrical signals in response to electrochemical reactions. The reactions typically scale with the surface area of the electrodes i.e., higher surface area provides higher reaction sites are available for an electrochemical reaction. However, increasing the surface area of the electrode more often leads to increased size of the sensor. In order to realize a sensor with a small size while maintaining a high surface area for electrochemical reactions, the ratio of the surface area to volume needs to be increased. In addressing this need, nanoporous structures are becoming popular in realizing a high surface area while maintaining a small size of the sensor. To realize nanoporous structures, MEMS has been identified as a technology to achieve most of the ideal requirements [16]. This is because the MEMS technology allows accommodating the scaling laws, for example fabricating nanoporous electrodes using advanced process techniques such as atomic layer deposition (ALD). Therefore, it is possible to realize high performance electrochemical devices that could be applicable in medical systems such as sensors for asthma detection.
1.3 Wafer-level fabrication and packaging of electrochemical devices

Wafer-level packaging is a method to package a device while it is still at the wafer-level, as compared to dicing the device from the wafer followed by individual packaging. Several methods are available for wafer-level packaging, one of the popular method used in realizing MEMS devices is by bonding a device wafer with a cap wafer [17]. Wafer-level fabricated and packaged electrochemical devices have been studied in realizing glucose sensors [18]. In this method, the electrodes of the sensors are fabricated on a Pyrex wafer and then anodically bonded to a silicon wafer containing microneedles with flow through channels.

1.4 Asthma diagnosis and a vision for hand-held measuring instrument

Asthma is a medical condition that is characterized by an inflammation of the airways of the lungs [20-22]. Inflammation of the airways is predominantly caused by air pollution and airborne pollen grains [23, 24]. A pictorial description of a normal airway and an airway during an attack is shown in figure 1.1. Due to the inflammation, the airways in the

Figure 1.1: Airways of lungs under normal condition and during an asthmatic attack. An asthmatic patient has a constricted airways and higher production of nitric oxide (NO) along the airways. From [19].
lungs release nitric oxide (NO) gas, the concentration of which is used to pre-determine the level of inflammation [21, 25-29]. A concentration of NO above 50 parts-per-billion (ppb) in adults typically indicates the presence of an inflammation [30, 31]. The standardized procedures indicate that the steady state nitric oxide gas concentration from exhaled breath is obtained when the breath is exhaled at a flow rate of 50 mlps and lasts for 10 s [32]. Ideally, a sensor should detect ppb-level nitric oxide gas concentration and respond within 10 s for detecting asthma. In addition, the sensor needs to be selective to interfering gases that are present in the exhaled breath, such as carbon monoxide (CO) and ammonia (NH₃). Furthermore, the sensor needs be able to operate at a high humidity since the exhaled breath contains humidity close to 100 %RH. These parameters of the sensor are ideal to be applicable in an asthma measuring instrument.

[Figure 1.2: Image of a child breathing into an asthma detecting instrument. The image gives an indication of the size of the instrument. From [33].]

Commercially available sensors detect nitric oxide concentration with a ppb-level sensitivity and has response time of the order of 40-60 s [34]. The implication of a slow response on a NO measuring instrument is undesirable. A typical NO measuring instrument that is available in the market is shown in the figure 1.2, which shows a child holding the measuring instrument with his hands [33, 35]. It can be observed that the measuring instrument is considerably large and requires both hands to hold the instrument. One of the reasons, for bigger size of the instrument, is the long response time of the nitric oxide sensor used in the instrument. Due to the long response time, the instrument needs to buffer the exhaled breath sample i.e., the instrument stores the exhaled breath in a reservoir and then pumps to the NO gas sensor at a slower rate. This requires the instrument to have gas sampling and handling systems to buffer and pump the sample, which results in a large
size of the instrument. Other methods of measuring NO using a potentiometric sensor and indirect conversion of NO has been demonstrated [36-38]. Although this has shown promising results for breath samples, the applicability to asthma monitoring is currently not validated with studies on several patients.

In order to realize a hand-held instrument, the size of the measuring instrument should be small so that patients can carry along with them. One of the objectives addressed in this thesis is the development of a miniaturized and fast sensor that eliminates the need for buffering of the breath sample. MEMS technology offers an efficient way to manufacture the sensors at a wafer-level, by using wafer-level fabrication and packaging of sensors. Therefore, a cost effective, hand-held, real time health monitoring system can be envisioned, and exhaling the breath into a mobile phone would enable to determine asthma in a real time mode.

1.5 Objectives of this thesis

This thesis presents research in the field of MEMS and specifically in the area of electrochemical sensors and their method of fabrication. The objective of this thesis is (a) to give a background to the electrochemical sensors and materials (b) to describe a novel method for temporary wafer handling of a thin wafer (c) to introduce fabrication of functional nanoporous membranes relevant for electrochemical sensing, and finally (d) to describe the development of a novel MEMS based gas sensor relevant for asthma and bad breath monitoring.

1.6 Thesis structure

For the sake of coherence the text in the thesis is organized using the general structure as detailed below.

In chapter 2, electrochemical concepts of gas sensing and temporary wafer handling are presented.

In chapter 3, the application of electrically induced adhesive for temporary wafer handling is described.

In chapter 4, fabrication of a highly porous functional material using atomic layer deposition (ALD) is described.

In chapter 5, the design and development of novel MEMS based gas sensor relevant for asthma and bad breath monitoring is described. Furthermore, integration and miniaturization of a novel MEMS based gas sensor is presented and its applicability to hand-held instruments is discussed and finally, chapter 6 concludes this work.
Chapter 2

Background to electrochemical sensors and materials

In this chapter, a brief introduction to amperometric sensors is presented. The working mechanism and the components that are used in an amperometric gas sensor are discussed. In addition, an introduction to the materials and properties of an electrochemically active adhesive is presented.

2.1 Introduction

Detection of gases involves several methods; some of them are listed in table 2.1. Among the various detection methods, amperometric detection has distinct advantages, i.e. high sensitivity, fast response time and high selectivity. In addition, it can be developed using materials that are commercially available which leads to low cost sensors as compared to other type of sensors. Although metal oxide sensors can be fabricated using a simple process method, their slow response, cross interference to other gases and high power consumption constitute considerable drawbacks [39, 40].
Table 2.1: Gas sensing types and principles

<table>
<thead>
<tr>
<th>Type</th>
<th>Principle</th>
</tr>
</thead>
<tbody>
<tr>
<td>NDIR sensor [41]</td>
<td>Target gas absorption coefficient, comparison</td>
</tr>
<tr>
<td>Catalytic gas sensor [42]</td>
<td>Resistance change measurement after reaction with the catalytic bead</td>
</tr>
<tr>
<td>Fluorescence sensor [43]</td>
<td>Detection of wavelength change of the fluorescence</td>
</tr>
<tr>
<td>Acoustic wave sensor [44]</td>
<td>Change in the resonant frequency</td>
</tr>
<tr>
<td>Amperometric sensor [45, 46]</td>
<td>Measurement of change in the working electrode current</td>
</tr>
</tbody>
</table>

One of the first amperometric gas sensor was reported by Qlark in the mid-1950s to monitor dissolved oxygen content in blood [47]. As shown in figure 2.1, the gas sensor consisted of two electrodes, electrolyte and a semi permeable membrane. The oxygen gas diffuses through the semi permeable membrane, and thereafter the electrolyte before reaching the working electrode. The thickness of the semi-permeable membrane controlled the diffusion of oxygen to the working electrode.

Figure 2.1: Schematic representation of the Qlark sensor, an amperometric sensor that was developed to detect oxygen. From [47].
Following this, amperometric sensors evolved to include a semi permeable membrane as the control element to select specific gases. Modern amperometric gas sensors employ three electrodes with reference electrode as the third electrode that allowed accurate control of the potential to the working electrode [45, 48, 49].

Currently, the research on amperometric gas sensors is typically divided into two fields. One field focuses on increasing the surface to volume ratio of the working electrode in order to realize a small geometric footprint with a high surface area electrode [50-52]. In the second field, the research aims at increasing the operating lifetime of the sensor by e.g. replacing the conventional acidic/basic electrolyte with ionic liquid electrolytes [46, 53, 54].

2.2 Amperometric gas sensor

In this section, the working principle and a brief overview of the main components of an amperometric sensor are presented. In addition, analytical characteristics of a gas sensor are described.

2.2.1 Working principle

The working principle of an amperometric gas sensor for detection of nitric oxide gas is illustrated in figure 2.2. Detection of the gas involves three major steps. In step 1, the sample gas containing the target gas (NO) is transported to the sensor either by diffusion or by pumping. In step 2, the gas diffuses to the working electrode, where NO undergoes oxidation. The electrons generated by the reaction at the working electrode result in a current that is directly proportional to the gas concentration. In step 3, the reaction products are diffused away from the electrode surface. If the reaction products remain on the electrode surface, it decreases the number of active surface sites for reaction and hence leads to a lower sensitivity. This effect is termed as poisoning of the electrode.
Therefore, a major consideration has to be given to the design of the working electrode of the sensor in terms of choice of geometry and composition of materials. A detailed investigation of a type of working electrode, i.e. gas diffusion electrode (GDE) is presented in the next section.

2.2.2 Gas diffusion electrode

An electrochemical reaction (oxidation or reduction) of a gas occurs at the interface between the working electrode, electrolyte and the gas, called as the triple phase point. Typically the working electrode of a sensor is composed of noble metals due to their inertness to chemical reactions or of carbon embedded with noble metals such as Platinum (Pt).

For NO gas, the solubility and diffusivity in liquid electrolytes is poor. For example, in aqueous electrolyte at 20 °C, the solubility of NO is approximately 1.94 mM/atm [55] whereas the solubility of O₂ is approximately 0.3 mM/atm. The low solubility of NO severely inhibits its transport through the electrolyte towards the electrode. Hence, an optimum design of the working electrode would provide an efficient transport path of the gas towards the electrode minimizing the diffusion length of the gas in the electrolyte.

The geometry of a gas diffusion electrode (GDE) allows electrochemical reaction to occur at a three phase point minimizing the diffusion length of the gas in the electrolyte.
Figure 2.3 (a) and (b) shows a cross section of a typical GDE and the three phase zone formed in a GDE. It consists of a narrow space in the electrode for the diffusion of gas and interaction with the electrolyte. At the three phase point, the effective concentration of the gas becomes sufficient to sustain a high current density [56]. Porous working electrode provides with large number of three phase points.

Figure 2.3 Three phase points in a gas diffusion electrode. (a) Cross section of a single pore of an electrode showing the electrolyte, gas and the reaction zone. (b) Concept of a three-phase point at an electrode. From [56].

One of the earliest gas diffusion electrodes was developed by Schmidt in 1923 who used a porous layer of platinum black that was electrolytically deposited on a hollow piece of carbon [57]. Over the last decade, gas diffusion electrodes have gained renewed interest in terms of design and development, especially for gas sensors and fuel cells [58-61]. In fuel cells, GDEs are used for both working and counter electrodes whereas in gas sensors it is mainly used as a working electrode.

The following section gives a detailed description of the components of an amperometric sensor namely filters, electrodes, electrolytes and potentiostat.
2.2.3 Sensor components

Figure 2.4 shows a schematic illustration of a three electrode amperometric gas sensor. A brief description of the components that are used in the sensor is given in this section.

![Figure 2.4: Schematic illustration of an amperometric gas sensor and its components. The three electrodes together with an electrolyte are sealed inside a plastic casing. The output pins are used for biasing the electrodes and to record the current from the working electrode.](image)

**Filter:** Filters in gas sensors mainly have the following purposes:

- Decrease poisoning of the electrodes
- Enhance the selectivity
- Reduce aqueous electrolyte loss
- Increase sensor life time

In addition, the filter also protects the sensor from an external hazardous environment. Several types of gas permeable filters exist. Typical filters include very thin layer (~20 um thick) of micro-porous Teflon film, PTFE modified porous films [62] or silicone films. Thickness and durability of the filter can be selected depending on the choice of the application. Filters can also be employed to remove unwanted gases by impregnating it with a gas sensitive chemical. For example, NO₂ gas can be selectively removed from a mixture of NO and NO₂ gas by using a filter dipped with triethanolamine [63].
Moreover, the filter controls the evaporation of the liquid electrolyte, i.e. using a thick filter leads to slow evaporation of the electrolyte. Therefore, an optimally thick filter would allow a low rate of electrolyte evaporation without sacrificing the gas diffusion time.

*Working electrode:* The electrochemical reaction of nitric oxide gas occurs at the working electrode resulting in a current proportional to the concentration of the gas. Several kinds of NO sensitive electrodes have been reported in the literature and have recently been commercialized [64, 65]. Four different approaches can be identified in developing NO sensitive electrodes. A first and popular approach is using a modified Clark type electrode, in which a thin layer of electrolyte separates a semipermeable membrane and the working electrode. In this approach, the O$_2$ permeable membrane of the Clark type sensor is replaced with an NO permeable membrane such as chloroprene [66], nitrocellulose [67] and silicone rubber [68] to make the sensor NO sensitive. A second approach (GDE approach) consists of coating a NO selective polymer directly on the surface of the electrode. For example, coating of Nafion or cellulose acetate polymer on the electrode surface has been used [69]. Electrocatalysis of NO by a modified iridium or palladium layer can be classified as the third type of NO sensitive electrode [70]. Finally, the fourth type of approach, which is commercially popular, is to use glassy carbon electrodes as the working electrode for NO sensors [71, 72].

*Electrolyte:* The function of the electrolyte is to support redox reactions, efficiently carry ionic current, and most importantly providing a stable reference potential to the reference electrode. It should also provide temperature stability, wide operating potential range and low viscosity. Four types of electrolytes exist: aqueous, non-aqueous, solid polymers and ionic liquids. A list of different electrolytes that have been used for gas detection is given in table 2.1.
Table 2.1: Few examples of electrolytes. From [73, 74]

<table>
<thead>
<tr>
<th>Type</th>
<th>Electrolytes</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Aqueous electrolytes</strong></td>
<td><em>Acid</em>: sulphuric, perchloric, phosphoric, HCl, HNO₃, acetic acid</td>
</tr>
<tr>
<td></td>
<td><em>Base</em>: NaOH, CsOH, LiOH, KOH</td>
</tr>
<tr>
<td></td>
<td><em>Neutral and salt</em>: KCl, LiCl, LiBr, NaHCO₃, acetate.</td>
</tr>
<tr>
<td><strong>Non-aqueous</strong></td>
<td><em>Solvents</em>: propylene, carbonate, DMSO, DMF, acetonitrile, ethylene glycol,</td>
</tr>
<tr>
<td></td>
<td>dichloromethane, propylene glycol, pyridine, THF</td>
</tr>
<tr>
<td><strong>Solid polymers</strong></td>
<td>Nafion, PEO*LiX, PVA/H₃PO₄, PVA/CsOH, and Inorganic Solids, ZrO₂</td>
</tr>
<tr>
<td><strong>Ionic liquids</strong></td>
<td>[Bmim][NTf₂], [Emim][NTf₂] etc</td>
</tr>
</tbody>
</table>

Potentiostat: One of the main advantages of an amperometric gas sensor is the low operating voltage and current ranges. Typically gas sensors with aqueous electrolytes operate between 0 and ±1.2 V with a current of few hundred nanoamps. Therefore, a simple printed circuit board (PCB) potentiostat can be used for measuring the current from the working electrode, as well as applying the bias voltage ($V_b$) between the working electrode (WE) and reference electrode (RE). Figure 2.5 shows a simplified schematic of the potentiostat.

![Figure 2.5: Schematic of a PCB based potentiostat connected to a three electrode gas sensor. Two operational amplifiers (OP1 and OP2) are used to measure the current from the working electrode and to bias the reference electrode, respectively.](image)
Two operational amplifiers OP1 and OP2 are connected to the electrodes of the gas sensor as illustrated in the figure 2.5. Operational amplifier OP1 is a transimpedance amplifier that converts the working electrode current to an output voltage, i.e. \( V_{\text{out}} = I_{\text{WE}} \cdot R_f \), where \( R_f \) is a resistor typically of few MΩ. Operational amplifier OP2 regulates the voltage at the reference electrode by maintaining the current, \( i=0 \). OP2 also acts as a current sink to the counter electrode. Thus, a constant bias voltage between the WE and RE can be maintained. Further details about the construction of a PCB based potentiostat can be found in [75]. An integrated programmable chip, LMP 91000 from Texas Instruments can also be used to construct a potentiostat [76].

2.2.4 Sensor characteristics

An amperometric gas sensor has the following characteristics:

- The gas concentration is proportional to the working electrode current, and is recorded between the working and the counter electrodes while maintaining a constant potential at the working electrode.
- The combination of the geometry for gas exposure, electrolyte confinement, electrode material and the electrochemical method (potentiometric or amperometric) determine the sensitivity and selectivity of the sensor.
- Low cost, small size and low power consumption are the most interesting characteristics of an amperometric sensor.

The three important parameters that are commonly used to assess the quality of an amperometric gas sensor are the sensitivity, selectivity and response time.

**Sensitivity:** Sensitivity of a gas sensor is the ratio between the working electrode currents and the respective gas concentrations. In practice, the sensitivity is thus determined from the slope of a plot of the working electrode current as a function of the gas concentration. The sensitivity of the gas sensor can be physically controlled by modifying the surface area of the working electrode. Diffusivity of the gas in the electrolyte affects the sensitivity of the sensor. In addition, filters, membranes and other sealing objects can influence the sensitivity.

**Selectivity:** Selectivity of a gas sensor is its ability to sense the desired gas while being insensitive to other interfering gases. The selectivity to undesired gases is obtained by choosing the type of electrochemical reaction of the target gas i.e., either oxidation or reduction. For example, in a mixture containing NO and NO₂ gas, it is possible to selectively oxidize NO gas. Selectivity based on kinetics depends on the electrode material and its catalytic behavior to the gases. For example, CO gas undergoes fast oxidation on Pt electrode, whereas it is \( 10^3 \) to \( 10^6 \) times slower on the Au electrode [73]. Thus, the sensor
can be made selective by choosing the right electrode material. Selectivity can also be obtained by using appropriate filter membranes designed for a particular gas (See section 2.2.3 for further details).

Response time: The advantage of an amperometric gas sensor is its ability to detect gas within few seconds. The response time of an amperometric sensor is mostly limited by the diffusion of the gas to the working electrode. For sensors applicable to the medical field such as breath analysis (e.g. CO, NO, O₂), the response time needs to be few seconds or less [32]. A response time of < 1 s for NO gas using a silicon based sensor was reported by Tierney et al. in which a direct diffusion path for the gas was designed [77]. A comprehensive analysis of the response time of an amperometric gas sensor can be found in [78].

2.3 An electrochemical adhesive for bonding and debonding

This section of the chapter presents the working principle of an electrochemically active adhesive used for the bonding and debonding of two electrically conductive substrates.

2.3.1 An electrochemically active adhesive: ElectRelease™

ElectRelease™ (EIC laboratory, USA) is a thermosetting adhesive that was initially developed for bonding and debonding of aluminum parts typically used in food and beverage packaging industries and for interactive packaging solutions [79-81]. The debonding process also works for a number of metals including aluminum, steel, low alloy steel, stainless steel, copper and titanium [81]. In this work, ElectRelease™ H23 was applied to wafer fabrication processes due to its low viscosity and its ability for slow cross-linking of the adhesive after mixing. The slow cross-linking time allows for several fabrication process steps such as adhesive dilution, spin coating and wafer alignment that are needed for pre-bonding of wafers. A photograph of the ElectRelease™ H23 adhesive is shown in figure 2.6, which contains a base and a hardner in separate tubes.
2.3.2 Principle of bonding and debonding

In practice, the two parts of the adhesive are mixed in the ratio of 4 (base):1 (hardner). The composition of the H23-base contains silicone fluid, bisphenol-A, epoxy resin, PEG-n-diglycidylether and salt (NH₄PF₆). The composition of the H23-hardner contains mercaptan and amines [82]. The hardner is an initiator of the cross-linking process of the adhesive. Once the cross-linking occurs, the adhesive mixture has a matrix functionality and an electrolytic functionality. The matrix functionality helps to adhesively bond to a substrate, whereas the electrolytic functionality provides the ionic conductivity between the substrates. A schematic illustration of the adhesive morphology before and after curing is shown in figure 2.7.

Figure 2.7: Schematic representation of the adhesive morphology before and after curing. The phase separation of PDMS-graft-PEG comb polymer in nanostructured epoxy resin. From [83].
Three basic steps of bonding and debonding of metal substrates, typically aluminum, using ElectRelease™ adhesive are illustrated in figure 2.8. In step 1, the adhesive is applied to one of the substrate, then joined to the other substrate and allowed to cure either at elevated temperature or at room temperature. In step 2, a voltage typically in the range of 10-50 V is applied to the metal substrates. At room temperature, the debonding of the substrates is induced when a voltage of 45 V is applied for 10 s or at 15 V for 20 min [84]. In step 3, the metal substrates are debonded manually. Normally, the adhesive remains in the cathode part leaving the clean anode part [84, 85].

![Figure 2.8: Illustration of the debonding technique using the ElectRelease™ adhesive.](image)

A comprehensive experimental investigation using surface analytical techniques to understand the mechanisms of debonding of the electrochemically active adhesive can be found in [83, 86-88]. In short, four possible processes at aluminum (anode) - adhesive interface that leads to debonding were identified i.e. anodic undermining, blistering debonding, osmotic blistering and anodic oxidation. One or a combination of several processes could be identified as the cause of debonding of substrates.
2.4 Discussion

Electrochemical sensors such as amperometric gas sensors have distinct advantage over other gas sensors in terms of high sensitivity, high selectivity and fast response time. Amperometric sensors can be sensitive to very low (< 25 %RH) or very high humidity (>80 %RH) changes. On the other hand, for most of the operating region, amperometric sensors seem to be promising device to detect and measure gas concentrations. The combination of the MEMS technology and amperometric detection of gas can potentially offer low cost sensors. Further research in the direction of increasing the life time of the sensor would be desirable. The properties of the electrochemically active adhesive and the debonding mechanisms have been presented. Four possible mechanisms were identified for debonding adhesively bonded substrates. The debonding of the substrates could likely be caused by one or more mechanisms involved in the debonding process.
A novel method for temporary handling of a thin silicon wafer

In the previous chapter, a brief introduction to an electrochemically active adhesive and the method for bonding and debonding of two metal substrates were presented. In this chapter, the application of an electrochemically active adhesive to thin silicon wafer handling will be described.

3.1 Introduction

The progress in the packaging of individual IC dies has evolved from a simple ‘wire bonded’ packaging to a complex 3D-IC packaging realized using through silicon vias (TSVs) as shown in figure 3.1. Next generation highly miniaturized and complex IC systems such as MEMS based CMOS image sensors would be developed using 3D-IC integration in which TSVs are a key enabling technology. Emerging applications such as photonics based on silicon interposers are also being developed for products in smartphone and tablets [89]. A silicon interposer is made from a thin silicon wafer in which TSVs are used to connect two or more functionalities in a die. The latest implementation of this technique can be found in Xilinx FPGA virtex 7 SSI (stacked silicon interconnect) device incorporating a thin silicon wafer interposer with TSVs as shown in figure 3.2.
Figure 3.1: Illustration of a roadmap in the progress of packaging of dies. TSV’s would be the enabling technology for the integration of several functionalities on a single die. From [90].

Figure 3.2: Cross section SEM image of Xilinx Virtex 7 SSI device incorporating thin silicon wafer (interposer) with TSVs to connect FPGA with the packaging substrate. From [91, 92].

One of the methods of fabricating TSVs is by etching vias followed by deposition of a conductive material to make the vias conductive, and thereafter thinning the silicon wafer.
Hence, this process involves handling of a thin silicon wafer which is often less than 50 µm in thickness. Thin silicon wafer are highly flexible and thus fragile. Therefore, a reliable solution is needed for handling such thin silicon wafers without causing any damage.

Handling of a silicon wafer can be carried out by adhesively bonding the wafer (device wafer) to be thinned to a thick silicon wafer (carrier wafer). In that way, the carrier wafer is used as a support. Three main process steps are involved in this method. They are bonding, thinning and debonding.

**Bonding:** Several types of polymers have been investigated for the use in adhesive wafer bonding; including epoxies, thermoplastics and photoresists [93-97]. For temporary bonding in wafer handling applications, both bonding and debonding properties of the adhesive are important. The adhesive should withstand the mechanical and thermal processes that are part of the, for example, TSV fabrication processes [98]. An efficient process of bonding requires the adhesive to be uniform and should allow the device wafer to be released from the carrier wafer without any damage [99, 100].

**Wafer thinning:** There exists four processes for thinning a wafer: mechanical grinding, chemical mechanical polishing (CMP), wet etching and dry etching [101]. Mechanical grinding is often used for thinning a wafer due to its high rate of thinning and low cost. However, this method of thinning process leads to a rough surface on the wafer [102]. CMP is often used in combination with mechanical grinding to polish the grinded wafers. Isotropic wet etching of silicon is typically done using a HNA solution (HF: Nitric acid: Acetic acid). However, it is difficult to maintain a constant etching rate over the entire surface, hence difficult to get a uniform final thickness [103]. Dry etching (Plasma based Reactive Ion Etching) in combination with CMP allows for a better control of wafer thickness [104]. Combinations of several methods are also prevalent to get a highly uniform surface of the silicon wafer [105].

**Debonding:** In one of the methods of debonding, the adhesively bonded wafer stack is heated to an elevated temperature for the adhesive to soften and become liquid [106-110]. The device wafer is then released by sliding it off from the carrier wafer. However, one drawback of this method is the high temperature (>200 °C) needed for debonding. Also, sliding a thin device wafer from the carrier wafer may damage the device wafer. In another method, the carrier wafer is coated with two types of adhesives having different bond strengths, as for example in the Zone bond™ technique [111]. In this technique, one type of adhesive with low bond strength is applied to the center of the wafer and another type of adhesive with higher bond strength is applied the edge of the wafer. The adhesive with higher bond strength is removed by a solvent treatment followed by mechanical delamination of the device wafer. This method requires several time consuming processing
steps. Laser ablation of a polymer sacrificial layer is another method in temporary wafer handling [112-115]. This method was used in controlled transfer of dies between two wafers using, e.g. polyimide or PET as an adhesive for manufacturing low-cost AFM devices [116, 117]. Table 3.1 summarizes few methods and causes of adhesive debonding.

Table 3.1: Methods of adhesive bonding and causes of adhesive debonding. From [108, 114, 118-120].

<table>
<thead>
<tr>
<th>Methods of bonding</th>
<th>Causes of debonding</th>
<th>Thermal stability (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thermal release tapes</td>
<td>Heat induced</td>
<td>80-130</td>
</tr>
<tr>
<td>Thermoplastic adhesive</td>
<td>Chemically dissolved</td>
<td>150</td>
</tr>
<tr>
<td>Thermosetting adhesive</td>
<td>Voltage induced</td>
<td>150-200</td>
</tr>
<tr>
<td>Photothermal polymer</td>
<td>Laser ablation</td>
<td>150-200</td>
</tr>
</tbody>
</table>

Thermosetting adhesive is a promising material for adhesive debonding since the bonding and debonding properties can be modified without difficulty. Several articles and patents are available describing the formulations with debonding properties [121]. In the next section, a thermosetting adhesive that enables controlled debonding of a thin wafer will be described.

3.2 Temporary wafer handling

In this work, ElectRelease™ H23 a thermosetting adhesive was utilized for the temporary wafer bonding of a thin silicon wafer. Figure 3.3 illustrates the fabrication process that was developed for temporary wafer handling. In summary, the ElectRelease™ adhesive was diluted with cyclopentanone (CPT) to get a low viscosity adhesive solution. This adhesive solution was spin coated on the carrier wafer in a similar way to a photoresist spin coating. The device wafer was then manually placed above the spin coated carrier wafer. The resulting wafer stack was transferred to the wafer bonding tool for bonding two wafers. Thereafter, the device wafer of the resulting wafer stack was thinned from 100 µm to 40 µm using RIE etching. In order to assess the applicability of this adhesive for temporary wafer handling, bond strength experiments on the prepared wafer stack were carried out and are described in the next section. For more processing details please refer to paper A.
Figure 3.3: Illustration of the fabrication process flow for bonding a device wafer to a carrier wafer with ElectRelease™ H23 electrochemical polymer adhesive. (a) Metal deposition on the device wafer. (b) Spin coating on the carrier wafer with diluted ElectRelease™ H23 adhesive solution. (c) Illustration showing the arrangement of the wafer stack after adhesive bonding of the aluminum coated device wafer. (d) Photograph of the bonded stack showing the electrical contact area of the device wafer which is exposed at the carrier wafer flat. From [paper A].
3.3 Wafer bond strength experiment

Two different types of silicon device wafers were investigated for debonding. One of the device wafers was sputtered with a thin aluminum layer and the other was a highly doped silicon wafer.

3.3.1 Metallized silicon device wafer

To enable the bond strength experiment before and after switching ‘ON’ the voltage, the wafer stack was fixed to a 3 mm thick aluminum plate providing an electrical contact to the carrier wafer. A UV release tape was attached to the device wafer to facilitate debonding and “peel-off” evaluation experiments. To measure the bond strength of the adhesive before switching ON the voltage, a dynamometer was attached to a corner of the UV tape and pulled upwards, thereby exerting a pull force on the attached device wafer as illustrated in figure 3.4(a). The photograph in figure 3.4(b) shows a high bond strength of the electrochemically active adhesive, since the UV tape is peeled off without releasing the device wafer.

![Diagram of test set-up for measurement of bond strength]

**Figure 3.4:** (a) Illustration of the test set-up for measurement of bond strength. (b) Photograph showing the force that is applied to the UV tape attached to the device wafer, measured with a dynamometer. The inset photograph shows the close-up of peeling of the UV tape from the device wafer. From [paper A].
Thereafter, a constant voltage of +50 V was applied between the device (anode) and the carrier (cathode) wafers as shown in figure 3.5(a). The voltage was switched off when the corresponding current density decreased to 1 mA/cm$^2$. The bond strength was measured again and it was now possible to debond the device wafer from the carrier wafer with a force of only 0.5 N, leaving the ElectRelease™ adhesive on the carrier wafer (figures 3.5(b) and 3.5(c)).

Figure 3.5: (a) Illustration of the evaluation set-up for measurement of bond strength after applying a voltage. (b) Illustration of the debonding procedure after applying a voltage. (c) Photograph showing the debonding of the device wafer when a force is applied to the UV tape attached to the device wafer. From [paper A].
3.3.2 Highly doped silicon device wafer

A highly doped silicon wafer was used as the device wafer in order to investigate the ability to debond without a conductive surface coated on the device wafer. A comprehensive description of the wafer bond strength experiment is given in paper A. In this section, shear force measurement on one of the wafer stack before and after voltage application is presented.

Figure 3.6: Illustration of the shear force measurement set-up for shearing of the bonded and released wafer stack, respectively. From [paper A].

Figure 3.6 illustrates a cross-section of the shear test set-up with the mounted wafer stack. The bond strength of the wafer stack was measured before and after applying a voltage using the shear tester. The measured shear force plots of the wafer stack before and after applying the voltage to the stack are shown in figure 3.7. The plots show the measured force on the shear head as a function of the shear head displacement. The shear head displacement represents the distance that the device wafer has moved from its initial position relative to the carrier wafer. Before applying a voltage, the bonded wafer stack could withstand the maximum possible shear force of the shear tester of 490 N. The achieved bond strength of more than 490 N demonstrates once more the high bond strength of the ElectRelease™ adhesive. After a voltage of 50 V was applied to the wafer stack, a second shear test was performed. The device wafer was sheared off at an applied shear force of 163 N.
3.4 Discussion

For the first time a novel approach for temporary wafer handling of a thin silicon wafer using an electrochemically active adhesive was successfully demonstrated. Two types of device wafers were investigated. In one type of the experiment, a non-conducting device wafer was coated with aluminum layer and in the other type, a highly doped silicon wafer was used as the device wafer. The advantage of using this technique with an aluminum coated device wafer is that the device wafer does not have to be conductive itself, for example a glass wafer can be used instead. In contrast, the advantage of using a highly conductive device wafer is that the post processing step of etching aluminum is avoided. Processing on the device wafer after bonding of the wafer stack is an important issue, which potentially could have an effect on the bond strength of the adhesive and the debonding process. However, the post bonding process, i.e. device wafer thinning by RIE etching, did not show any signs of premature debonding. Damages or cracks in the thin device wafer were not observed after the debonding process concluding that the adhesive withstood the RIE etching of the device wafer.

The presented method could become a breakthrough for several applications. Interactive packaging of IC dies in which, the IC dies can be tested and discarded merely by applying a voltage between the test platforms is an area of application that is gaining interest. In addition, photo-patternning of the adhesive would open up new areas in the field of selective debonding mechanism. In the future, thin wafer handling can also find its use in fabrication of gas sensors in which highly porous working electrodes are fabricated on a thin device wafer that are then transferred by debonding to another wafer containing reference and counter electrodes.
Chapter 4

Functional nanoporous material using atomic layer deposition

This chapter describes a method to fabricate a functional nanoporous material from a silicon substrate by coating dual layers of platinum (Pt) and aluminum oxide (Al₂O₃) using atomic layer deposition (ALD). The nucleation delay & film growth properties of Pt and Al₂O₃ on different types of substrates are discussed. Future prospects and applications of such fabricated functionalized nanoporous materials are presented.

4.1. Introduction

Functional nanoporous materials have been a subject of interest and studied extensively in the last decade [122-126]. In electrochemical sensors, in particular gas sensors, nanoporous materials allow for higher sensitivity. This can be ascribed to the inherent increased surface-to-volume ratio of the nanoporous material leading to an increased line length of the triple-phase point interface [127-132]. Functional nanoporous material can be fabricated by depositing thin layers of desired materials on a nanoporous substrate, e.g. porous alumina. Atomic layer deposition (ALD) is identified as a promising tool to achieve the goal of depositing thin layers of materials on nanoporous substrates.
Atomic layer deposition enables to deposit metals and dielectrics on the surface of a substrate with a precise thickness. A schematic illustration of an ALD process is shown in figure 4.1. The process consists of a reaction between the precursor gas (Pulse:A) and reactant gas (Pulse:B) at a given temperature and pressure. During the Pulse: A, the precursor gas flows into the reaction chamber of the ALD and chemisorbs on the surface of the substrate forming a monolayer of molecules. An inert gas such as argon is then purged to remove the excess precursor materials. During the Pulse:B, the reactant gas flows into the reaction chamber and interacts with the monolayer of the precursor molecules. The reactant gas undergoes a reaction with the precursor molecules forming a monolayer of metallic or dielectric material on the surface of the substrate. Finally, an inert gas is purged through the reaction chamber to remove the reaction products and excessive reactant molecules. Thus, one complete ALD cycle results in one monolayer of the material being deposited on the surface of the substrate. By controlling the precursor and reactant gas pressure and time duration, materials can be deposited in narrow crevices and pores that allows for the development of nanoporous materials.

Figure 4.1: Atomic layer deposition process. Pulse A: precursor gas pumped to the ALD chamber. Pulse B reactant gas pumped to the ALD chamber resulting in a reaction product that leaves a monolayer of desired material.

Two methods of ALD are prevalent: thermal ALD and plasma enhanced ALD (PEALD). The thermal ALD process is based on dissociative chemisorption of the precursor by a reactant at the surface of a substrate [133]. On the other hand in PEALD, the surface of the substrate is treated with a plasma during pulse:B cycle in order to oxidize the precursor monolayer as compared to thermal ALD where water or oxygen is often used during the pulse:B. Table 4.1 compares the thermal ALD and PEALD. PEALD is advantageous as compared to thermal ALD due to the increased mass density of the
deposited material and faster growth per cycle. Hence, the precursor cycle times can be made shorter when PEALD is used. However, most importantly, the conformality of the deposited material is better in thermal ALD due to the formation of smaller grain size. Hence, thermal ALD is useful in depositing materials in narrow corners, crevices and pores. Therefore, in this work, thermal ALD was selected for fabrication of functional nanopores. An extensive study of various precursors for different materials has been carried out by George [134].

Table 4.1: Comparison of thermal and plasma ALD. From [135-137].

<table>
<thead>
<tr>
<th></th>
<th>Thermal</th>
<th>Plasma</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass density of the material</td>
<td>+</td>
<td>++</td>
</tr>
<tr>
<td>Growth per cycle (GPC)</td>
<td>+</td>
<td>++</td>
</tr>
<tr>
<td>Precursor cycle times</td>
<td>Short</td>
<td>Shorter</td>
</tr>
<tr>
<td>Conformality</td>
<td>Better</td>
<td>Limited</td>
</tr>
</tbody>
</table>

4.2. Fabrication of functional nanopores

In this section, fabrication of nanoporous material using an anodic aluminum oxide (AAO) substrate is described. In addition, the process of functionalization by depositing two layers of materials using ALD on open ended nanopores is presented.

4.2.1. Method to create open ended nanopores

AAO substrate fabrication: A 525 µm thick single side polished Si wafer with a 400 nm thick SiO\textsubscript{2} layer was used as a substrate, on which 1 µm thick aluminium layer was deposited. The aluminium layer was anodized to form a 1.4 µm thick regular pore array with 25 nm diameter and 75 nm pitch (figure 4.2). The anodization was carried out by Synkera Technologies Inc., Logmont CO, USA.
Substrate processing: In brief, the back side of the silicon wafer was lithographically developed with 6 mm diameter circular patterns, which was then etched to a depth of approximately 440 μm (figure 4.3(a)). In order to have a supporting grid structure to the AAO layer, a second photolithography step was carried out (figure 4.3(b)). A triangular grid with 20 μm wide and 120 μm long beams was etched from the remaining silicon on the backside wafer cavity (figures 4.3(c) & (d)). The grid structure was necessary to ensure a mechanical stability to the AAO structure. At this point, the wafer was diced to 10 mm × 10 mm chips (figures 4.3(e) & (f)).

Barrier layer etching: The diced chip now consists of three layers: the porous AAO layer, the barrier layer of the AAO layer and the silicon dioxide layer. The silicon dioxide layer below the barrier layer was etched. To create an open ended nanoporous substrate, the barrier layer has to be etched as well. This barrier layer is a thin compact Al₂O₃ layer at the bottom of the porous AAO. Most commonly used method to remove Al₂O₃ layer is by using H₃PO₄ (5 wt%) solution [138]. However, this method would take approximately 50-90 mins. Etching of the barrier layer should be done with caution since overetching the barrier layer may damage the nanopores. In this work, a recipe was developed to successfully dry etch the Al₂O₃ barrier layer with an etch gas composition of Cl₂ with 20 sccm, BCl₃ with 2 sccm and Ar with 20 sccm at 600 W, for approximately 60 s. Thus, an open ended nanoporous AAO membrane suspended on a grid was successfully
developed (figure 4.3(f)). In the next section, a model and the recipe for functionalization of the nanoporous membrane using ALD are presented.

Figure 4.3: Fabrication flow and SEM images of the AAO substrate at different process steps: a) and b) The AAO film is formed on a Si substrate. Cavities are etched in the substrate from the bottom and the grid is patterned on spray coated photoresist; c) and d) The grid is etched from the backside in the Si until reaching the buried SiO$_2$ layer. The AAO surface is protected with a photoresist layer before dicing. The inset shows the closed end of the AAO pores; e) and f) After dicing, the buried SiO$_2$ and the Al$_2$O$_3$ barrier layer is etched on chip level to open the AAO membrane. The inset shows the pores now open at the bottom. From [paper B].
4.2.2. Dual layer ALD: A predictive approach

*Figure 4.4: Schematic illustration of a nanopore during ALD deposition. The spheres represent the precursor gas molecules forming a progressing monolayer until saturation of the pore surface. From [paper B].*

**Model:** Figure 4.4 shows a schematic illustration of a nanopore during ALD deposition in which \( L \) indicates the length of the pore and \( d_{\text{pore}} \) is the diameter of the pore. For a successful ALD deposition in deep nanopores, it is necessary to ensure the saturation of the whole surface, including deep inside the pores with the precursor/reactant molecules. This requires that the exposure times (precursor pulse and the reactant pulse) are sufficiently long. A small pulse duration would result in a partially covered pore wall and if the pulse duration is too long there could be a wastage of precursor/reactant gases [139].

The saturation dose, during the film growth, \( S_s \), is typically \( 10^{15} \) [molecules cm\(^{-2}\)] [140-142]. This depends on the material surface, on the pressure applied and on the type of the gas, i.e. the chemisorption of the first few monolayers of gas or vapour molecules depends on weak surface forces. The exposure required for sidewall coverage derived in paper B is given by:

\[
\delta = S_s \sqrt{\frac{2 \pi m k T}{P_{\text{pore}}}} \left( L + \frac{3 p L^2}{32 A_{\text{pore}}} \right) \text{[Langmuir, L]} \quad \ldots (2)
\]
where \( m \) is molecular mass of the precursor, \( k \) is the Boltzmann constant, \( T \) is the temperature in kelvin and \( p \) is the precursor partial pressure. This equation is often corrected with a sticking coefficient, \( \alpha \), in the denominator to account for non-ideal saturation of the surface, where \( \alpha \) is expressed as the percentage of the surface covered with a monolayer of the precursor. It is also known that, for some materials, there is a delay in the formation of the first monolayer and is called as the nucleation delay. This phenomena can also be corrected by \( \alpha \). This nucleation delay is known to be particularly long for Pt [143], but no exact value of the sticking coefficient has been reported for Pt to date. We note that \( \alpha \) was also reported to vary with temperature [144]. The derived model predicts an initial condition for the exposure of the precursor and reactant gases. The purging gases should ensure that any non-chemisorbed molecules or any reaction products present in the reactor are removed to make the surface suitable for the next reaction and to ensure the self-limiting surface growth process [145, 146].

**Recipe**: The deposition of Pt results from the reaction of MeCpPtMe\(_3\) (precursor) with O\(_2\) (reactant). The deposition of Al\(_2\)O\(_3\) is the product of trimethylaluminium (TMA) reacting with H\(_2\)O. Starting from the exposure value predicted by the theoretical model (see above), the deposition parameters (i.e. exposure and number of cycles) needed to be further tuned to achieve a uniform deposition in these high aspect ratio nanopores (60-80 nm diameter with a length of 1.4 \( \mu \)m). The tuning of the thickness of the deposited layer was achieved by varying the number of cycles. Tables 4.2(a) and (b) give the recipes that were used for the deposition of Pt and Al\(_2\)O\(_3\) in nanopores, respectively. For example, to deposit approximately 10 nm thick platinum on a Al\(_2\)O\(_3\) substrate, 250 cycles were required.
Table 4.2 (a): Recipe parameters for the deposition of Pt in deep pores.

<table>
<thead>
<tr>
<th>Deep-pore ALD recipe for Pt deposition</th>
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</thead>
<tbody>
<tr>
<td><strong>Cycle steps:</strong></td>
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<tr>
<td><strong>Process temperature:</strong></td>
</tr>
<tr>
<td><strong>Precursor pulse</strong></td>
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<tr>
<td></td>
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<tr>
<td></td>
</tr>
<tr>
<td><strong>Purge 1</strong></td>
</tr>
<tr>
<td><strong>Reactant pulse</strong></td>
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<tr>
<td><strong>Purge 2</strong></td>
</tr>
</tbody>
</table>

Table 4.2 (b): Recipe parameters for the deposition of Al₂O₃ in deep pores.

<table>
<thead>
<tr>
<th>Deep-pore ALD recipe for Al₂O₃ deposition</th>
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<tbody>
<tr>
<td><strong>Cycle steps:</strong></td>
</tr>
<tr>
<td><strong>Process temperature:</strong></td>
</tr>
<tr>
<td><strong>Precursor pulse</strong></td>
</tr>
<tr>
<td><strong>Purge</strong></td>
</tr>
<tr>
<td><strong>Reactant pulse</strong></td>
</tr>
<tr>
<td><strong>Purge</strong></td>
</tr>
</tbody>
</table>

In order to assess the nucleation delay and film growth properties, deposition of Pt and Al₂O₃ was also conducted on several planar substrates. It was found that Pt film growth starts after 125 cycles on Al₂O₃ substrate and after 150-160 cycles on SiO₂. However, on a bare silicon wafer that was etched with HF and immediately transferred to the reaction chamber, hardly any growth was observed. On the other hand, it was observed that Al₂O₃ deposition starts immediately on any given surface. These observed differences can be
inferred to different surface adhesion properties. If the substrate is oxidized, the chemisorption properties are enhanced and lead to quick formation of a monolayer of the ALD material. Further explanation of the characterization process is given in paper B.

To summarize, there are several challenges that should be addressed when developing a recipe for an ALD. One of the main challenges is the estimation of the exposure required for each precursor. In this section, a method to estimate the exposure and number of cycles for deposition of materials in high aspect ratio nanopores was presented.

4.3. Discussion

In recent times, there has been a lack of development of AAO based devices. This could be predominantly due to the bottom-up approach of the technology, i.e. fabrication of a nanostructured template followed by material deposition and finally device development. The top-level is highly complex and is also perhaps very interesting. In this chapter, a successful method to create a wafer-level fabricated nanoporous membrane that is functionalized with two layers of materials using atomic layer deposition was presented. The fabrication of functionalized nanopores at a wafer-level has a vast potential to create novel materials that could be useful in high density capacitors, fuel cells and electrochemical sensing. In particular, functional nanoporous material with Pt layer could be promising for high sensitivity gas sensing application due to high surface area to volume ratio of the material.
Chapter 5

Wafer-level fabrication of amperometric gas sensors

Introduction to asthma and the role of nitric oxide in asthma were presented in chapter 1. In this chapter, the design and the development of a highly sensitive and fast response amperometric NO gas sensor that is potentially applicable for asthma monitoring is described. The sensor consists of three electrodes that act as working, reference and counter electrodes, respectively. The oxidation of nitric oxide gas at the working electrode causes a current flow between the working and the counter electrodes that is proportional to the gas concentration. Furthermore, the developed amperometric sensor was redesigned and successfully tested for hydrogen sulphide gas concentrations that are relevant for bad breath monitoring.
5.1 Introduction to the design of a nitric oxide sensor

The following design parameters were considered when developing the sensor: (1) a highly porous gas diffusion working electrode, (2) ease of fabrication, (3) ease of assembly, (4) ease of integration with a potentiostat and (5) possibility for scaling of the sensor. Based on these design criteria, a novel nitric oxide gas sensor was successfully fabricated and characterized. The design of a three electrode NO sensor that includes working, reference and counter electrodes is shown in figure 5.1. In an attempt to fabricate a high sensitivity sensor, a microporous grid structure was etched in the silicon. This microporous grid was coated with platinum and Nafion™ and then was used as a working electrode. A voltage bias ($V_{\text{bias}}$) of +0.7 V was applied to the working electrode as compared to the reference electrode using a potentiostat connected to the sensor. An accepted reaction occurring at the anode due to the oxidation of nitric oxide can be written as [147].

$$NO + 2H_2O \rightarrow NO_3^- + 4H^+ + 3e^- ; \quad …\quad (3)$$

![Figure 5.1: Schematic of the designed amperometric sensor. The microporous working electrode was fabricated using a 300 µm thick silicon wafer. Silver sputtered on a polycarbonate board was used as the counter and reference electrodes. 5 % wt $H_2SO_4$ was used as an electrolyte solution. From [Paper C].](image)
5.2 Fabrication and assembly of the nitric oxide sensor

Among the design criteria listed above, the development of a porous working electrode was of importance. The working electrode of the sensor was fabricated by following a standard MEMS fabrication process. The detailed processing steps can be found in paper C. In summary, a microporous working electrode was first realized by DRIE etching a 300 µm thick silicon wafer. A platinum layer of thickness 10 nm was deposited using ALD on the surface of the microporous grid as described in chapter 4. Thereafter, Nafion™, a semipermeable nanoporous membrane, was dip coated on the microporous grid and dried. This successfully resulted in a highly nanoporous working electrode.

To form the counter and reference electrodes, a silver of thickness 500 nm was sputter deposited on a polycarbonate board, which was then demarcated using a milling machine. All the electrodes were assembled using silicone adhesive glue to form an amperometric sensor. A polycarbonate board with meandering channel was realized in order to keep the sensor filled with electrolyte (5 wt % H₂SO₄) as shown in figure 5.2.

![Figure 5.2](image)

**Figure 5.2:** Schematic cross section of the assembled amperometric sensor with meandering electrolyte channel. The inset photograph shows an assembled nitric oxide sensor. From [Paper C].
5.2.1 Measurement set up and instrumentation

A measurement system was set-up for characterizing the amperometric sensor. The schematic diagram of the measurement set up is shown in the figure 5.3. A 200 ppb NO gas concentration was used as a calibration gas for testing the sensor. The calibration gas was diluted with N₂ gas to obtain several NO concentrations in order to assess the sensitivity of the sensor. The gases were humidified using a humidifier which consisted of a syringe inserted with a moistened tissue paper. A potentiostat was used to measure the current from the working electrode of the nitric oxide sensor. A Labview™ script was developed to record the experimental parameters, i.e. gas flow, humidity and temperature.

Figure 5.3: Schematic diagram of the measurement set-up used for characterizing the amperometric gas sensor. The data from the flow sensors and the humidity sensor was recorded using a LabVIEW script. From [Paper D].

5.2.2 Characterization

The analytical properties of the sensor such as stability, sensitivity, selectivity, settling time, response to humidity and flow were measured using the measurement set-up described in the previous section. More detailed information about the sensor characterization can be found in paper C. In this section, two important properties of the sensor, namely sensitivity and settling time, together with a model for the settling time will be presented and its relevance to asthma monitoring will be discussed.
**Sensitivity and settling time:** In order to assess the sensitivity of the sensor, the output current of the sensor ($I_{NO}$) was measured for different concentrations of NO gas as shown in figure 5.4(a). The sensor was able to detect NO concentrations with sensitivity of 0.045 nA/ppb and in the ppb-level range that corresponds to the concentration range of the NO in asthma monitoring. Jacquinot et al also reported a NO sensor with ppb-level sensitivity. However, to be applicable for hand-held instruments, the large size and discrete components of their sensor were not suitable [148].

![Figure 5.4 (a): The distribution of NO sensitivity for five different sensors. One of the sensors with filter is illustrated by the (-.-) straight line. From [Paper C].](image)

The settling time of the sensor was measured by alternately switching the flows of the gases between NO and N$_2$ as shown in figure 5.4(b). The settling time was calculated to be approximately 8 s. In order to predict the sensor settling time in a real measurement condition of asthma monitoring, i.e. with an exhaled breath as the input to the sensor, a sensor model was also developed.

![Figure 5.4 (b): Response of the sensor when the NO gas was alternately switched between 0 to 200 ppb resulting in a settling time of approximately 8 s. From [Paper C].](image)
Sensor model: The transfer function model of the NO sensing system that was used to predict the sensor settling time is shown in figure 5.5. The exhaled breath transfer function was obtained from the NO measurement of exhaled breath reported in [22] as shown in figure 5.6(b). The sensor characteristic transfer function was derived from the experimentally measured response of the sensor (figure 5.4). The response of the sensor was simulated by following the procedure in figure 5.5, with the exhaled breath transfer function as the input to the sensor model. This resulted in a critically damped output response which had a settling time of approximately 7-8 s (figure 5.7). From this, it was inferred that the sensor could reach a stable output for a given NO concentration within 7-10 s time window. It should be noted that the physiologically relevant NO concentration obtained from the exhaled breath reaches a stable value after approximately 7 s (figure 5.6(b)) [22, 32]. Therefore, it can be inferred that the experimentally obtained settling time of the NO sensor could be applicable for real time exhaled breath measurements.

\[
\text{Exhaled breath transfer function (sensor input): } \quad \frac{1}{1.2s + 1}
\]

\[
\text{Sensor characteristic transfer function: } \quad \frac{1}{0.3s^2 + 0.4s + 1}
\]

\[
\text{Settling time (sensor output): } \quad \sim 7-8 \text{ s}
\]

Figure 5.5: A transfer function model for NO sensing system. The exhaled breath transfer function serves as the input to the sensor transfer function. The sensor characteristic transfer function allows determining the settling time of the sensor.
Figure 5.6: Exhaled NO schematic diagram. (a) The peak concentration of NO occurs when the subject has inhaled through the nose. (b) NO measurement from the exhaled breath. Adapted by permission from Macmillan Publishers Ltd: Immunology and Cell Biology [22], copyright 2001.

Figure 5.7: Sensor output model when exhaled breath is introduced to the sensor. The output from the sensor is found to be stable and lies within the required 10 s duration. It can be inferred that the designed sensor can be used for real time measurements.

5.3 Integrated and miniaturized nitric oxide sensor

In section 5.2, a working prototype of a nitric oxide sensor that measured ppb-level concentration was described. The settling time and the sensitivity were found to be appropriate for the sensor to be applicable in an asthma detecting instrument. However, the sensor lacked a proper design for electrolyte supply which, resulted in its large size (figure 5.2). In addition, the manual assembly of the working, reference and counter electrodes is not well suited for a large scale manufacturing of the sensor. A hand-held gas sensing instrument could be envisioned with a miniaturized and highly sensitive sensor that has fast response time. One of the methods to achieve this would be to fabricate the sensors at a wafer level integrated with liquid electrolyte.

One of the first silicon based nitric oxide amperometric gas sensor with integrated electrodes and electrolyte was reported in [149], a schematic representation is shown in the figure 5.8. It consisted of a gold working and counter electrodes with a silver reference electrode and the electrolyte used was Nafion™ gel. Holes of 2 µm diameter were etched in the silicon using DRIE, on which electrode materials were sputtered to form working, reference and counter electrodes, respectively. Nafion™ gel, which is used as an
electrolyte, was applied manually on the electrodes. Nitric oxide gas was exposed from the substrate of the device. This design was reported to have a response time of less than 0.5 s. However, the sensor had a detection limit of 5 ppm, which is too high for asthma detection.

Figure 5.8: One of the first amperometric gas sensor fabricated using silicon as the substrate with integrated electrodes and electrolyte. Nafion™ gel was used as the electrolyte. From [149], © 2011 IEEE.

5.3.1 Sensor design and fabrication

The sensor design idea was to integrate all the electrodes on a single chip with a liquid electrolyte packaged inside this chip. To realize such an integrated sensor, a SOI wafer was used for fabrication of the microporous working electrode. The counter and reference electrodes were fabricated on a glass substrate which was then anodically bonded to the SOI wafer. The cavity formed between the SOI wafer and the glass wafer was used for electrolyte storage. A 3D illustration of the fabricated integrated NO sensor is shown in figure 5.9.
The device wafer of the SOI was etched to form a microporous grid structure and the carrier wafer of the SOI was etched to form a cavity. To realize the working electrode platinum was deposited using ALD on the microporous grid structure. The reference and the counter electrode were realized by depositing a 500 nm thick silver layer on the glass wafer. The SOI wafer with working electrode was anodically bonded to the glass wafer containing counter and reference electrodes. Thus, an integrated sensor was developed as shown in figures 5.10(a) and (b). The dimension of the sensor after dicing is approximately $10 \times 10 \times 1$ mm. In order to integrate the electrolyte, the sensor was dip coated with Nafion and then allowed to dry at room temperature followed by filling with 5 %wt H$_2$SO$_4$ electrolyte. A detailed explanation of the fabrication process can be found in paper: D.
5.3.2 Analytical properties

Sensor characteristics of the integrated sensor were determined by measuring the sensitivity and the response time. The average value of the output current measured at different concentrations is shown in figure 5.11(a). The output current ($I_O$) was found to be linear with the NO gas concentration. From the slope, a sensitivity of 0.04 nA/ppb was calculated, which is in agreement to the sensitivity of the nitric oxide sensor with discrete components.
Response time of the sensor was measured in a similar way to the non-integrated sensor by alternately switching NO gas concentration between 0 and 200 ppb. The response time was calculated using $t_{90}$, of the average final value of the output current which resulted in approximately 12 s as shown in figure 5.11(b).

5.3.3 Operating life time

The operating life time of the sensor is dictated by the volume of the electrolyte present in the sensor. The evaporation of the electrolyte from the sensor was measured to be approximately 2 h when the sensor surface was exposed to the ambient air. In order to further improve the sensor packaging, one of the challenging tasks is to minimize the evaporation of the electrolyte. Several possible methods were investigated including replacing the liquid electrolyte with a non-aqueous electrolyte such as solid polymer electrolyte (Nafion™), ionic liquid (Emim NTF2) and glycerin (100% pure). With ionic liquid and glycerin the ppb-level sensitivity was not achieved. With Nafion as a solid electrolyte, it is well established that the sensor could become humidity dependent, which is undesirable [150].

Currently, commercial sensors employ multiple layers of Teflon™ based membrane to prevent the evaporation of the electrolyte. One of the drawbacks of this method is an
increased response time (> 50 s) of the sensor and hence may not be applicable for real
time asthma monitoring.

One of the proposed solutions to prevent the evaporation without sacrificing the
response time was to use a mechanical sealing module, described in paper D. Using this
module, it was estimated that the sensor would need approximately 30 s of measurement
time for one measurement of NO concentration which, would enable approximately 200
measurements until the electrolyte in the sensor evaporates. It could be envisioned that an
electrically controlled actuator for the opening and closing of the sealing mechanism can
be included for the asthma monitoring application.

5.4 Integrated and miniaturized hydrogen sulphide sensor

The integrated sensor was characterized for hydrogen sulphide (H\textsubscript{2}S) gas which is a
component of the oral breath that causes bad breath. H\textsubscript{2}S gas is predominantly used as one
of the biomarker for bad breath/Halitosis monitoring. The sensor was found to be sensitive
to H\textsubscript{2}S gas in the ppb-level range when the bias voltage between the reference and the
working of 1.1 V was applied. Interference to NO and NH\textsubscript{3} gases that are commonly found
in the oral cavity was experimentally verified and found that the sensor was selective to
these gases. Further characterization details can be found in paper E.

5.5 Discussion

Research and development of amperometric gas sensors has spanned over several decades.
Amperometric gas sensor has evolved from a two electrodes sensor for sensing oxygen, to
a stable three electrode gas sensor that is able to sense several gases. The wafer-level
fabricated sensor with integrated electrodes and liquid electrolyte presented in this chapter
is a technological leap from a commercially available canister based design to a SOI-glass
based design. It is possible to envision a highly sensitive gas sensor that can be
manufactured in large volumes. The research presented in this chapter of the thesis is in
the direction of an integrated and miniaturized sensor that can applied to a hand held gas
monitoring device.

In the near future, a mobile phone carrying a miniaturized gas sensor would allow
personalized asthma diagnosis by merely exhaling the breath into the phone. With this, a
hand-held health monitoring system that is able to track the medical condition of an
individual can be envisioned.
Chapter 6

Conclusions

This thesis has presented research in the field of MEMS and specifically in the area of electrochemical sensors and their method of fabrication. A novel method for temporary handling of a thin device wafer was demonstrated. A successful fabrication process for developing functional nanoporous membranes relevant for electrochemical sensing was described and finally, a brief description of the wafer-level fabricated MEMS based electrochemical sensors that are relevant for medical diagnostics was presented. The following conclusions can be derived from the research presented in this thesis.

- A method for temporary handling of thin wafer using an electrochemically active adhesive was demonstrated. A wafer could be bonded, thinned and debonded without any damage. This method has the potential to facilitate handling of thin wafers with structures such as nanoporous materials or through silicon vias (TSV’s). The metallization process that is required for the nonconductive device wafer opens up new opportunities in handling glass wafers.

- A novel functional nanoporous material with dual layers of materials was successfully designed and fabricated. The fabrication process involved successful deposition of dual layer materials along the side walls of the deep nanopores. Thus fabricated functional nanopores can be potentially applied in electrochemical sensing, fuel cells, as a filter membrane and many other myriads of ubiquitous devices. Furthermore, the fabrication process developed at a wafer-level, demonstrates the ability to manufacture nanoporous membrane in large volumes.
A MEMS based novel amperometric gas sensor that is sensitive to ppb-level nitric oxide gas concentration was successfully demonstrated. The gas sensor featured a combination of a high surface area microporous electrode and nanostructured Nafion™ coated along the side walls of the micropores. A miniaturized sensor with a dimension of $10 \times 10 \times 1$ mm with integrated electrodes and a liquid electrolyte was designed and developed. A hand-held medical instrument such as asthma monitoring instrument based on the designed sensor can be envisioned. Furthermore, the amperometric sensor was redesigned and successfully tested for ppb-level hydrogen sulphide gas concentrations which are relevant for bad breath monitoring.

To summarize, the electrochemical sensors and fabrication methods presented in this thesis makes a shift in the paradigm of the development of a hand-held monitoring and diagnostic instruments for medical applications. This leads us to conclude that in the future, a comprehensive measurement system such as personalized health monitoring device using mobile phones could be envisioned.
Summary of Appended Papers

**Paper A: Temporary wafer bonding and debonding for 3D integration using an electrochemically active polymer adhesive**

The use of thin silicon wafers is an enabling technology for 3D integration in the semiconductor industry. However, thin silicon wafers are fragile to handle and reliable solutions are required for thin wafer handling. This paper reports a novel method of bonding and debonding a thin wafer (<50 μm) using an electrochemically active polymer adhesive. In the presented method the carrier wafer is first spin coated with the adhesive and then bonded to the device wafer by applying force and temperature. Debonding of the wafer is realized at room temperature by applying a voltage between the carrier and the device wafer, which substantially reduces the bond strength. The bonding and debonding properties of the adhesive show that temporary wafer bonding using electrochemically active adhesives has the potential to be an attractive approach for temporary wafer bonding for thin wafer handling in 3D integration processes.

**Paper B: Pt–Al₂O₃ dual layer atomic layer deposition coating in high aspect ratio nanopores**

Functional nanoporous materials are promising for a number of applications ranging from selective biofiltration to fuel cell electrodes. This work reports the functionalization of nanoporous membranes using atomic layer deposition (ALD). ALD is used to conformally deposit platinum (Pt) and aluminum oxide (Al₂O₃) on Pt in nanopores to form a metal–insulator stack inside the nanopore. Deposition of these materials inside nanopores allows the addition of extra functionalities to nanoporous materials such as anodic aluminum oxide (AAO) membranes. Conformal deposition of Pt on such materials enables increased performances for electrochemical sensing applications or fuel cell
electrodes. An additional conformal Al$_2$O$_3$ layer on such a Pt film forms a metal–insulator–electrolyte system, enabling field effect control of the nanofluidic properties of the membrane. This opens novel possibilities in electrically controlled biofiltration. In this work, the deposition of these two materials on AAO membranes is investigated theoretically and experimentally. Successful process parameters are proposed for a reliable and cost-effective conformal deposition on high aspect ratio three-dimensional nanostructures. A device consisting of a silicon chip supporting an AAO membrane of 6 mm diameter and 1.3 $\mu$m thickness with 80 nm diameter pores is fabricated. The pore diameter is reduced to 40 nm by a conformal deposition of 11 nm Pt and 9 nm Al$_2$O$_3$ using ALD.

**Paper C:** *An amperometric nitric oxide sensor with fast response and ppb-level concentration detection relevant to asthma monitoring*

A MEMS-based amperometric nitric oxide (NO) gas sensor is reported in this paper. The sensor is designed to detect NO gas for the purpose of asthma monitoring. The unique property of this sensor lies in the combination of a microporous high-surface area electrode that is coated with Nafion™, together with a liquid electrolyte. The sensor is able to detect gas concentrations of the order of parts-per-billion (ppb) and has a measured NO sensitivity of 0.045 nA/ppb and an operating range between 25 and 65% relative humidity. The settling time of the sensor is measured to 8 s. The selectivity to interfering gases such as ammonia (NH$_3$) and carbon monoxide (CO) was high when placing an activated carbon fiber filter above the sensor. The ppb-level detection capability of this sensor combined with its relatively fast response, high selectivity to CO and NH$_3$ makes the sensor potentially applicable in gas monitoring for asthma detection.

**Paper D:** *A wafer-level liquid cavity integrated amperometric gas sensor with ppb-level nitric oxide gas sensitivity*

A miniaturized amperometric nitric oxide (NO) gas sensor based on wafer-level fabrication of electrodes and a liquid electrolyte chamber is reported in this paper. The sensor is able to detect NO gas concentrations of the order of parts-per-billion (ppb) levels and has a measured sensitivity of 0.04 nA/ppb with a response time of approximately 12 s. A sufficiently high selectivity of the sensor to interfering gases such as carbon monoxide (CO) and to ammonia (NH$_3$) makes it potentially relevant for monitoring of asthma. In addition, the sensor was characterized for electrolyte evaporation which indicated a sensor operation lifetime allowing approximately 200 measurements.
**Paper E:** *An amperometric hydrogen sulphide sensor applicable for bad breath monitoring.*

A MEMS-based amperometric H\textsubscript{2}S Sensor relevant for bad breath detection is reported in this paper. The miniaturized wafer level fabricated three electrode amperometric H\textsubscript{2}S sensor is designed to detect Hydrogen Sulphide (H\textsubscript{2}S) gas of the order of parts-per-billion level relevant for bad breath measurement. The sensor has a measured sensitivity of 0.65 nA/ppb and a response time of approximately 21 s. The sensor was selective to NO and NH\textsubscript{3} gases that are normally present in the oral cavity of an adult.
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