Micro-hotplate for Integrated Thin-Film Gas Sensor

By

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Abstract

Micro-hotplate (MHP) provides a platform for thin-film gas sensor operating at elevated temperature. It is proposed elsewhere that temperature programmed desorption technique can be used to improve the selectivity of gas detection. For this reason, the temperature uniformity and the ease of controlling the operating temperature on a MHP become more and more important. In this thesis, the author intended to address the thermal management problem. In the first part of this work, the use of mechanical engineering software to simulate the thermal behavior of MHP is demonstrated. The simulation can be used to estimate the temperature distribution and heater power of the MHP under design. Next, a novel MHP structure is proposed. The approach uses frontside anisotropic etching of silicon together with special layout to create the thermally isolated structure. Sandwich of inter-dielectric layers and aluminum interconnection provides the supporting material while highly doped boron diffusion provides the heating and temperature sensing. The design incorporates guard heater layout that improves the temperature uniformity. Simulation result shows that the temperature variation on a sensor film of 50 \times 60 \, \mu m^2 is less than 25 \, ^\circ C when the operating temperature is 350 \, ^\circ C. The micro-hotplate fabricated exhibits heating efficiency of about 7 \, ^\circ C/mW and CMOS compatibility.

Finally, tin dioxide was identified as the gas sensing material and was deposited using RF reactive sputtering of tin under oxygen ambient. The film composition and grain structure have been characterized by XPS and STM techniques. We have also designed the preliminary schematic of an automatic gas sensor characterization system. With the foundation laid by this work, many research activities in integrated gas sensor such as gas sensitivities and selectivity investigation can be carried out.
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Chapter 1

Introduction

Microfabrication technology has been branching into sensors and actuators in the past decades. The incessant drive toward lower cost by batch processing has driven technologists to develop silicon based devices to replace the traditional solid-state devices. Micro-fabricated physical sensors such as pressure sensor and accelerometer have achieved better success in market place than chemical sensors thus far. Although the feasibility and advantages of micro-fabricated chemical sensors have been demonstrated, very few of them have been successfully commercialized. On the contrary, chemical sensors have a potentially large market in application such as domestic appliance, medical and health, automobile and environmental industries. Before the prototype devices resulted from academic research can be massively produced, various technical problems such as stability, package and testing must be solved. This opens up many research opportunities.

Micro-fabricated gas sensor has received much attention recently [1.1]. It has significant advantages over traditional one using thick-film based sensors. For example, the thin-film has higher sensitivity and better control in quality. Miniature device allows small sample size, low ohmic potential drop and fast response. Micro-machining technology, which enables the fabrication of thermally insulated structure, adds an extra advantage of low power consumption to micro-fabricated gas sensor. However, conventional integrated gas sensor based on pressure sensor structure introduces
unnecessary complication in fabrication. We intend to use standard CMOS technology as much as possible. We also address the thermal management problem of current devices by novel structure, layout and simulation. Our efforts have resulted in an integrated gas sensor that serves as the testing platform for gas sensor research in HKUST.

1.1 Overview of Gas Sensor Development

Gas sensors have the longest history among chemical sensors. Early at 1962, Taguchi [1.2] demonstrated the first tin oxide based chemical sensors. Six years later, the Figaro Engineering Inc. in Japan began the industrial production of SnO₂ semiconductor sensor based on thick film technology. The CO sensor was applied in LP gas leakage alarm and detection of automobile exhaust. In 1975, I. Lundström invented the hydrogen sensitive Pd-gate MOSFET [1.3]. The sensor has a very high sensitivity to hydrogen. It is also sensitive to ammonia. So far these are the two most important inventions in the gas sensor development.

Although other semiconductor metal oxide such as TiO₂ and ZnO₂ are also sensitive to reducing gas, tin oxide is the prime choice because chemically it is relatively stable. Doping can be introduced into tin oxide to selectively increase the sensitivity towards the gases of interest. For example, Al-doped sample is better detector for reducing agent and In-doped sample is better detector for oxidizing agent [1.4]. TiO₂ based gas sensor also appears in the market as NOₓ and oxygen sensor for freon leakage checker and automobile engine control respectively.

In the United States, more research efforts were concentrated on integrated silicon gas sensor technology. The work was pioneered by C. L. Johnson and K. D. Wise [1.5] who reported the first micro-machined integrated gas sensors in 1988. The device utilizes a selectively-etched dielectric window to provide the thermal insulation. The window has a heat efficiency of about 3°C/mW and a time constant of 10 msec. The fabrication process was originally developed for pressure sensor. We shall call the thermal insulation structure the "Micro-hotplate (MHP)". This device was applied in the detection
Fig. 1.1 Examples of micro-machined gas sensor. (a) shows the conventional one which is adopted from pressure sensor [1.5]. (b) shows a recently developed structure [1.10].

of gas purity in low-pressure systems such as reactive ion etching. The sensing material was a thin-film platinum. However, thin-film tin oxide is more attractive than any other materials because it was widely applied by the commercial thick-film sensor industry. There are many published papers related to the fabrication of thin-film tin oxide gas sensor on a similar micro-hotplate structure [1.6].

The recent trend of the research is to integrate array of sensors for gas selectivity improvement. This work was pioneered by Wang [1.7] and Wise [1.8]. Within a gas mixture, it is difficult to derive the concentration of individual gases from only one gas sensor. Therefore, an array of sensors which have divergent cross-sensitivities are required. Multivariate calibration algorithms such as artificial neural networks can be applied to calibrate the array system [1.9]. There are only few published works in this area and it leaves a lot of research opportunities in matching the right kind of sensor elements in the array.

It is very difficult to integrate circuit into the conventional micro-machined gas sensor (Figure 1.1a). The processing is not compatible with standard microelectronics technology. In 1993, Suehle [1.10] reported the first monolithic tin oxide gas sensor fabricated by commercial CMOS foundry fabrication (Figure 1.1b). Special post-fabrication processing techniques were used to complete the sensor. The conventional backside etching is replaced by front-side etching on specially aligned openings. This
method reduces the silicon etch time and requires no additional mask. The etch terminate
at intersected silicon (111) planes. The hotplate area is also significantly reduced.

1.2 Applications of Gas Sensor

Japan perhaps is the most active country in the world to drive gas sensor into commercial
applications [1.11]. The oldest application is the domestic gas leak detectors for LP gas.
Later, detector for town gas (CH₄, H₂ and C₂H₅OH) was also commercialized. The
specification of alarm gas concentration is about 300-500 ppm. Other applications include
gas sensor in air purifier, sensor (including humidity sensor, alcohol sensor and smoke
sensors) in microwave ovens control, odor checker for foodstuff testing, alcohol checker¹
and automobile engine control. The oxygen sensor for the last application is the largest
market in gas sensor. The total sale of oxygen sensor in Japan was ¥ 1,680 million (U.S.
17 million) in 1991 and is expected to grow rapidly. Applications in environmental
monitoring have not been fully explored. Gas exhaust from car is a serious pollution
problem in Hong Kong and inexpensive NOₓ sensor is in demand. Besides, the
government asserts a very low allowable limit of H₂S in city because of its harmfulness to
plant growth. Equipment in the order of million dollars is required to monitor the low
concentration of H₂S in the air. The possibility of replacing it by inexpensive solid-state
H₂S sensor should be explored.

1.3 Study on Gas Sensing Principle of Thin-film
Metal Oxide

Improvement of sensor performance cannot be achieved without a physical understanding
of the gas sensing process. There are many papers on the sensing principles but no
complete theory has been developed thus far. Deep understandings may require

¹ It is interesting to mention that the alcohol checker was developed by cooperation
between Figaro Eng. Inc. in Japan and ACS in Hongkong.
Fig. 1.2 Illustration to show the physical model and band diagram of space charge layer on grain.

background in the field of heterogeneous catalysis and semiconductor surface physics [1.12]. We shall provide a simplified physical description of the process [1.13].

1.3.1 Space Charge Boundary

For polycrystalline structure, the surface layer locates at the grain boundary as shown in Figure 1.2(a). Normally, the thin-film is exposed to air where the oxygen content is rich. Oxygen ions are adsorbed on the boundary which in turn bend the energy band. It causes a positive space charge layer as shown in Figure 1.2(b). The space charge layer is highly resistive because of the barrier height $V_s$. Magnitude of $V_s$ depends on the chemisorbed oxygen concentration. If the grain size is very small, the polycrystal resistance is dominated by the grain boundary resistance.
1.3.2 Influence of Reducing and Oxidant Gases on Conductance

Reducing gas will remove chemisorbed oxygen [1.12]. As the concentration of chemisorbed oxygen decrease, the intergranular barrier height will also decrease and account for the decrease in resistance. Typical Taguchi type sensors show a power law dependence of resistance on partial pressure of the reducing agent.

\[ R \propto [P]^{-S} \]  \hspace{1cm} [1.1]

where \( R \) is the sensor resistance, \( P \) is the partial pressure of the reducing gas and \( S \) is a constant. \( S \) is very close to 0.5 for thick-film sensor. This dependency was explained by Morrison [1.13]. It is expected that thin-film sensor also shows similar dependence. His model should be reviewed for thin-film sensor which the surface to bulk ratio is large.

Just as oxygen does, oxidant gases will increase the sensor resistance. It binds the electron in grain or surface boundary and increases the intergranular barrier height. One of the example is NO [1.14]. The surface reactions in the presence of NO and air is the following

\[ e^- + NO_{(gas)} + O_{(ads)} \rightarrow NO_2_{(ads)} \]  \hspace{1cm} [1.2]

The adsorbed species have a higher electro-negativity than chemisorbed oxygen and increases the barrier height.

1.3.3 Metal Catalysts

In many cases, metal catalysts are added to increase the response time, sensitivity and selectivity towards gas under interest. The catalyst may contribute by the following mechanisms [1.15]:

1. The catalyst lowers the activation energy of the reaction. The dissociation of hydrogen on platinum is an example of this type of reaction.

2. The catalyst activates organic molecules by ionizing the molecules or forming radical species.
3. The catalyst can provide a broad spectrum of surface sites (called heterogeneous surface). The surface sites will increase the reactive rate despite the loss of selectivity. One example is to use Pd on top of SnO$_2$ as a catalyst for the oxidation of hydrocarbons. The very thin layer of Pd forms small clusters and leads to an effectively high oxidation state for the metal with more oxygen available.

1.4 Problem Identification

In this work we shall focus on the engineering of the gas sensor. Thin-film type sensors find more applications than active device sensors such as gas sensitive MOSFET. Keeping in mind that it is very important to have a prototype device that will provide a platform for long term research in this area, we decided to concentrate on the device design and process development.

1.4.1 Micro-hotplate Design with Better Thermal Management

The thermal management of integrated gas sensor has not received much attention so far. Simple serpentine heater had been used by many people [1.10] [1.16]. Unfortunately, it produces a large temperature variation on the hotplate (Figure 1.3). The non-uniform temperature profile causes ambiguity of the sensor operating temperature. This non-uniformity will degrade the selectivity, sensitivity and reproducibility of the sensor. One approach to improve the selectivity is to use the sensor responses at different temperatures together with array signal processing [1.17]. Again the poor temperature uniformity imposes the same limitation.

1.4.2 Motivation for Thermal Simulation

Simulation tools for integrated sensor and actuator are always in demand. Simulation is necessary in order to verify the design without actually fabricating the device. Due to the complexity of the analysis, diversity of the problem, there is no successful simulation software in this area. We decided to use simulation tools from mechanical engineering.
Fig. 1.3 Example of temperature distribution of micro-hotplate using serpentine heater measured using an infrared microscope (after [1.18]).

1.4.3 Micro-hotplate Fabrication Compatible with Standard Technology

As discussed in section 1.1, early developed micro-hotplates are based on non-standard processing. For example, special metals (e.g. Pt) which has higher melting point are used instead of aluminum. The structures require backside processing which is not a standard conventional integrated circuit process. Suhle [1.10] was first to demonstrate the fabrication of integrated gas sensor using CMOS foundry. We believe there is still room to improve his structure.

1.5 Thesis Contribution

We summarize the major contributions of this thesis in the followings.

1.5.1 Thermal Simulation of Integrated Gas Sensor using Finite Element Analysis

For the first time, the use of finite element analysis was applied to simulate the thermal behavior of integrated gas sensor chip [1.19]. Mechanical engineering CAE/CAD packages PATRAN and ABAQUS were used to simulate published hotplate structures and also the structure proposed by us. The simulation has helped us to optimize the sensor design.
1.5.2 Novel Micro-hotplate Design and Fabrication

A new micro-hotplate structure for thin-film gas sensor was proposed [1.20]. The device was successfully fabricated. The fabrication process was significantly simplified. It is also compatible to standard processing technology. The sensor layout was considered carefully to improve the temperature uniformity. The design was verified by finite element analysis. Experimental result shows that the fabricated device exhibits high heating efficiency.

1.5.3 Sensor Fabrication and Characterization

With the deposition of gas sensing film on top of the micro-hotplate, we can investigate the gas sensitivity of the sensor. Tin dioxide was deposited using RF reactive sputtering of tin under oxygen ambient. The film composition and grain structure have been characterized. To measure systematically the gas sensitivity and dynamic characteristics of gas sensors, an automatic gas sensor characterization system is essential. We have designed the preliminary schematic of the system. Appendix B summarizes the design and operating principle of the system.

1.6 Summary

In this chapter we have reviewed the development of gas sensor technology and especially the micro-hotplate technology for thin film gas sensor. The sensing principle of thin-film metal oxide was summarized to give the reader some physical background. So far, the importance of thermal management on the sensor chip is not fully recognized. In our work, we have explored the application of finite element analysis to characterize the thermal behavior. With carefully designed layout and newly proposed structure, we fabricated a micro-hotplate with improved temperature uniformity. We have also developed a process to deposit tin oxide. We have designed an automatic gas sensor characterization system. With the fundation laid by this work, research activities in gas sensitivities and selectivity can be carried out. We believe that we have made a step towards a practical integrated gas sensor.
1.7 Reference


Chapter 2

Thermal Analysis

The thermal management of integrated gas sensor has not received sufficient attention thus far. The importance of temperature uniformity and the ability to sense accurately the operating temperature of the thin-film sensor have been overlooked. While integrated gas sensor aims at precision measurement of gas concentration, the operating temperature of the thin-film sensor should be uniform. Highly non-uniform temperature profile gives rise to ambiguity of the operating temperature. It will also degrade selectivity and sensitivity. Furthermore, the recovery of the sensor to baseline measurement can be a strong function of operating temperature [2.1]. Stability and life time of the sensor can be improved if the temperature is carefully controlled. Temperature control is even more important if temperature programmed desorption technique [2.2] is used in the gas detection. In catalytic work, it is known that a given gas will desorb at a characteristic temperature from a given film. By ramping the temperature, the conductivity shift at a given temperature should be a significant help in identifying the gases present in the ambient.

In chapter one (see Figure 1.3), it has been shown that improperly designed micro-hotplate will result in a temperature variation as high as a hundred degrees. Unfortunately, the problem is difficult to model analytically due to the three-dimensional nature. It is also difficult to measure the surface temperature on an integrated gas sensor chip experimentally. Therefore, numerical simulation is an acceptable alternative. The simulation result can help us to learn more about the structure. To our knowledge there is
no commercial simulation software that can be applied to the simulation of the mechanical and thermal behavior of integrated sensors and actuators. This is still an area of intense research [2.3]. This is a difficult task because the requirement differs from sensors to sensors. The lack of material property database for IC processing materials further complicates the task. We decided to use Mechanical Computer Aided Engineering (MCAE) software instead. PATRAN and ABAQUS are finite element based MCAE software packages for solving three-dimensional mechanical problems. We believe that this thesis is the first to report this type of work.

This chapter presents the simulation methodology and the simulation results on selected published structures. The first section covers basic concepts in performing the simulation. While it is too complicated to model all the geometrical details of the sensor structure, some assumptions must be made to simplify it.

### 2.1 Simulation Methodology

Finite Element Analysis programs PATRAN [2.4] and ABAQUS [2.5] are employed for the thermal analysis. PATRAN is an open-ended, general purpose, three-dimensional
Fig. 2.2 Illustration to show how the layout structure is modelled in the simulation. The diagonal lines of the heater in layout is converted to orthogonal lines. All the vertex are aligned on coarse grid.

MCAE software package that uses interactive graphics to link engineering analysis and results visualization. PATRAN does not provide a thermal analysis module. ABAQUS is a batch program that provides robust finite element analysis including thermal analysis. ABAQUS does not have a graphical interface. PATRAN is used extensively in the simulation except the finite element analysis. The finite element model created by PATRAN will be converted into ABAQUS input file. After the analysis by ABAQUS is completed, the result is imported to PATRAN for visualization. The simulation flow is illustrated in Figure 2.1.

2.1.1 Solid Modeling

The two-dimensional integrated circuit layout must be converted into a three-dimensional solid models. In the simulation, the entire model is built up from solids called hyperpatch. Here are some important points to be noted,

1. Hyperpatches of each material should have contiguous identity number to facilitate the material definition. They should be assigned with one unique color for clearness.

2. The hyperpatches should be topologically congruent (i.e. the elements along an edges of two hyperpatches are continuous). Otherwise, isoparametric meshing (refer to 2.1.2) cannot be applied.
It is impossible to model the physical structure exactly. Therefore significant simplification is applied to the simulating structure (see Figure 2.2). For example, the coordinates of the nodes are rounded off to coarse grid and some diagonal lines are converted into orthogonal lines. These simplifications will cause significant inaccuracy in the simulation. However we can not avoid the inaccuracy because of the limitation in the finite element analysis. Therefore we have to retain the important geometry as much as possible and interpret the result carefully. It also reminds us the importance of experimental verification (refer to 5.2.1).

2.1.2 Meshing

The meshing process generates finite elements from the hyperpatches. In PATRAN, it can only be done semi-automatically. User has to take care the continuity of the elements along the edges of the hyperpatches. If the hyperpatches are topologically congruent, a single mesh directive - "parametric mesh" can mesh the entire model. Otherwise, user has to manually specify the number or length of element along each edges. After the meshing, nodal equivalencing is executed to remove dummy nodes along patches' boundary. Element wavefront optimization is also performed to compact the node ID's so that the analysis time can be reduced. The mesh are now ready for analysis.

2.1.3 Material Property Definition

For static thermal analysis, only the thermal conductivity is required. ABAQUS allows the specification of temperature dependence of thermal conductivity. Table 2.1 shows the thermal conductivity of various materials used in the simulation. The data is extracted from traditional material handbook [2.6] [2.7]. Since the data are bulk parameters, it is not guaranteed that it can represent the property of corresponding thin-film layers. Furthermore, the simulation assumes the thermal conductivity of P+ resistor to be equal to that of bulk silicon. For more accurate simulation, these parameters should be experimentally measured for each process.
2.1.4 Boundary Condition

Boundary condition such as convection, radiation and heat source can be applied. The losses due to radiation and convection are negligible as compared with the conduction heat loss through the package. If the power is very small such that the bottom face of the die is essentially at ambient temperature, the temperature of the nodes at the bottom face can be set to ambient temperature $T_a$ without loss of accuracy. In this simulation, a heat transfer coefficient ($h_{ca}$) that represents the conduction heat loss to the package is assigned to the bottom face of the die.

$$h_{ca} = \frac{1}{\theta_{ca}A} \quad (2.1)$$

where $\theta_{ca}$ is the thermal resistance of the package and $A$ is the area of the bottom face of the die. $\theta_{ca}$ is assumed to be 110 °C/W (TO-5 package). The reference temperature of the heat transfer coefficient is the ambient temperature which is assumed to be 50°C. The heat source in terms of heat flux per unit volume is assigned to the heater elements. Here the simulation assumes uniform heat flux in the heater. Therefore, the power divided by heater volume gives the heat flux.

2.1.5 FEA

The analysis is carried out by ABAQUS. ABAQUS input file is generated by the PATABA module of PATRAN. The file includes the information about node, element,

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Si</th>
<th>Al</th>
<th>SiO2</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>1.56</td>
<td>2.37</td>
<td>0.0138</td>
</tr>
<tr>
<td>400</td>
<td>1.05</td>
<td>2.40</td>
<td>0.0150</td>
</tr>
<tr>
<td>500</td>
<td>0.80</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>600</td>
<td>0.64</td>
<td>2.31</td>
<td>0.0175</td>
</tr>
<tr>
<td>700</td>
<td>0.52</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>800</td>
<td>0.43</td>
<td>2.18</td>
<td>0.0217</td>
</tr>
</tbody>
</table>
Table 2.2  Simulation parameters for the thermal analysis of four integrated gas sensor structures.

<table>
<thead>
<tr>
<th>Case to ambient thermal resistance $\theta_{CA}$ (°C/W)</th>
<th>110</th>
</tr>
</thead>
<tbody>
<tr>
<td>Convective heat coefficient (W/m² °C)</td>
<td>30</td>
</tr>
<tr>
<td>Chip dimension (mm²)</td>
<td>3.6×3.6×0.25</td>
</tr>
<tr>
<td>Membrane thickness (µm)</td>
<td>5</td>
</tr>
<tr>
<td>Ambient temperature (°C)</td>
<td>50</td>
</tr>
</tbody>
</table>

material definition, boundary condition and the analysis. The generated file has some problems. We have written a simple program to fix the problems. The problems are described in the followings,

1. The heat transfer reference temperature is set to zero by PATABA. The program corrects it into the ambient temperature (50 °C).

2. We cannot define the temperature dependence of material property in PATRAN. Therefore, the program adds the temperature dependence data into the output file.

3. The analysis directive (*STEP) has improper parameters. The program corrects it into static linear thermal analysis.

4. Lastly in the node set definition of the output file, PATABA assumes the node identity do not exceed 5 digits. However, we do have node ID's more than 5 digits and the node ID's become contiguous in the output file. ABAQUS can not interpret the long ID and will exit with error. Therefore, the program inserts a space between any two ID's.

After the analysis is completed, the result file which contains the nodal temperatures are converted into PATRAN nodal result file using the ABAPAT module of PATRAN. At this point, PATRAN is ready to display the temperature contour using the nodal result file.
Fig. 2.3 (a) to (d) are the solid models used in simulation. The hatched area is the membrane and the crossed area is the heater.

2.2 Simulation on Published Sensor Structures

In this chapter, we shall discuss the simulation results on four integrated gas sensor chips. As pointed out earlier, the geometry detail is simplified. The structures are assumed to make up of silicon only. Radiation loss is ignored while natural convection loss is retained. Table 2.2 lists the parameters used in the simulation.

The four simulation structures as shown in Figure 2.3 are: (a) bulk structure with a pair of rectangular heaters, (b) membrane structure with area heater [2.8], (c) membrane structure with area and guard heater [2.9], and (d) integrated array of four membranes [2.10]. In the simulations, the active areas are heated up to about 250°C. Here the active area is defined as the area where the sensor element is located. The active area of structure (a) is the region between the heater pair while the active areas of structure (b) to (d) are assumed to be the heater region. Figure 2.4 shows the cross-section of the
membrane structures (b) to (d). The back-etched wall has a typical angle of 54°C. For the integrated array, the simulation only investigates the effect of heating one element.

Figure 2.5 shows the simulated temperature contours. Structure (a) has a rather isothermal surface ($\Delta T \approx -4^\circ C$ at 250°C) but it has a low heating efficiency. The bulk substrate cannot provide thermal insulation. Structure (b) has much higher heating efficiency due to the thermal isolation provided by the thin membrane. The drawback is that a severe temperature gradient exists across the active area of Structure (b) ($\Delta T \approx -100^\circ C$ at 250°C). The temperature gradient is the consequence of the heat flow from the membrane center to the edge of the membrane (see Figure 2.4), which is then dissipated to the ambient through the case. To have an isothermal active area, any heat flow in the active area plane should be minimized.

Hille [2.9] reported a two-heater arrangement. The first heater called the guard heater\(^1\), which just encloses the active area, supplies the heat loss to the ambient through the substrate and the package. A second heater called the area heater, which is placed in the active area, supplies the heat loss to ambient by convection. Structure (c) incorporates the additional guard heater and the simulation result looks satisfactory ($\Delta T = -5^\circ C$ at 250°C) except for some distortion at the corners.

\(^1\) It was originally named as ring heater by Hille. In some other cases as described later, this heater may not be a ring shape. The author has changed the name for more meaningful sense.
The area heater power $P_{\text{area}}$ can be expressed as [2.9]

$$P_{\text{area}} = h_c u^2 (T_O - T_A) \tag{2.2}$$

where $h_c$ is the convective coefficient, $u$ is the membrane side length (see Figure 2.6), $T_O$ and $T_A$ are the temperature of active area and ambient respectively. In most cases, $P_{\text{area}}$ is very small as compared with $P_{\text{guard}}$ and the area heater can be eliminated. For example, the convective loss of an active area of 1500$^2\mu$m$^2$ is only about 0.0675mW/°C (using Equation 2.2) which is very small as compared to the guard heater power. The guard heater power is dissipated to the ambient through the thermal resistances $\theta_{\text{OS}}$, $\theta_{\text{SC}}$ and $\theta_{\text{CA}}$ in series (see Figure 2.6). Here the subscripts $O$, $S$ and $A$ denote the edge of active area, substrate and the case respectively. Hille has solved $\theta_{\text{OS}}$ in term of $(1-a/u)$ ratio analytically where $a$ is the active area side length. Owing to the non-linearity caused by the dependence of thermal conductivity on temperature, the analytical solution is prone to error. In the following, the use of simulation to empirically calculate $\theta_{\text{OS}}$ is illustrated.

Figure 2.7 shows the simulated thermal resistances for different $(1-a/u)$ ratio. $\theta_{\text{SA}}$ is very close to $\theta_{\text{CA}}$ ( = 110°C/W from Table 2.2). Hence, we can conclude that $\theta_{\text{SC}}$ is negligible. Then the guard heater power can be calculated as

$$P_{\text{guard}} = \frac{T_O - T_A}{\theta_{\text{OS}} + \theta_{\text{CA}}} \tag{2.3}$$

The guard heater power can be minimized by using smaller $a/u$ and $h$ (see Figure 2.7). In integrated circuit applications, the substrate temperature should be kept low by using better heat sinking package and smaller heater power. For example, a package with $\theta_{\text{CA}}$ of 50°C/W requires $\theta_{\text{OS}}$ of 1.5°C/mW for a substrate temperature rise of 10°C at the operating temperature of 350°C.
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Fig. 2.5 Simulated temperature contours of structures (a) to (d).

Fig. 2.6 Cross-section of membrane with equivalent thermal resistances.
Fig. 2.7 Relationship between the thermal resistances in figure 2.5 and (1-a/u) ratio. The x, * and Δ character lines denote $\theta_{OA}$, $\theta_{SA}$ and $\theta_{OS}$ respectively.

2.3 Conclusion

Finite element analysis program PATRAN and ABAQUS are applied to analyse the thermal characteristic of integrated gas sensor structures. PATRAN performs the three-dimensional finite element modelling of the chip while ABAQUS performs the analysis. The analysis result is imported to PATRAN for visualization. The physical structure is significantly simplified in the model and the result should be interpreted with care. As illustrated in the simulation of four gas sensor structures, the simulation can be used to estimate the temperature distribution and heater power. It can be used to calculate the thermal resistances. In the Chapter 4, the same methodology is used to simulate a novel micro-hotplate structure.
2.4 Reference


Chapter 3

Process Development

We have developed the process for the anisotropic etching of silicon using Ethylene-diamine Pyrocatechol solution and the deposition of tin dioxide using reactive sputtering. The anisotropic etching is the critical step that forms the suspended micro-hotplate structure. The thin-film tin dioxide is the gas sensing material that is sensitive to reducing gases. This chapter gives an overview and describes the underlying principle of the process. The experimental setup and results will also be presented. Two sets of masks (IGS002 and IGS003) are designed for the fabrication of the integrated gas sensor. IGS003 is the improved version of IGS002. The layout design is explained in Section 3.3.

3.1 Anisotropic Silicon Etch

3.1.1 Overview

KOH (Potassium Hydroxide) and EDP (Ethylene-diamine-Pyrocatechol) are the common anisotropic etchants of silicon. EDP etch is perfectly masked by silicon dioxide thus makes it suitable for long etching. For this reason, EDP is chosen in this work. KOH exhibits much higher (110)-to-(111) etch rate ratios than EDP so that it is useful for vertical groove etching on (110) wafers. KOH is much cheaper and has a lower operating temperature. EDP is carcinogenic and should be handled with care. Currently, another anisotropic silicon etchant TMAH (Tetramethyl Ammonium Hydroxide) [3.2] is proposed. This etchant is quite attractive because of its non-toxicity and slow etch rate of aluminum.
Table 3.1: Comparison of EDP and KOH etchant characteristic (from [3.1]).

<table>
<thead>
<tr>
<th>Etchant</th>
<th>Typical Anisotropic (100)/(111) Etch Rate Ratio</th>
<th>Dopant Dependence</th>
<th>Masking Films (typical etch rate)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethylene diamine</td>
<td>35:1</td>
<td>(\geq 7 \times 10^{19} \text{ cm}^{-3}) boron reduces etch rate by about 50</td>
<td></td>
</tr>
<tr>
<td>Pyrocatechol</td>
<td></td>
<td></td>
<td>(\text{SiO}_2) (2A/min)</td>
</tr>
<tr>
<td>(water, pyrazine)</td>
<td></td>
<td></td>
<td>(\text{Si}_3\text{N}_4) (1A/min)</td>
</tr>
<tr>
<td>KOH</td>
<td>400:1</td>
<td>(\geq 10^{20} \text{ cm}^{-3}) boron reduces etch rate by about 20</td>
<td></td>
</tr>
<tr>
<td>(water, isopropyl)</td>
<td></td>
<td></td>
<td>(\text{SiO}_2) (14A/min)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(\text{Si}_3\text{N}_4) (1A/min)</td>
</tr>
</tbody>
</table>

However, due to lack of published data, TMAH is not chosen in this work. Table 3.1 compares the etching characteristic of EDP and KOH.

A brief discussion of the etching mechanism is given in the following. By understanding the mechanism, one can select the etching condition for a given etch rate, the amount of residue, anisotropy and the P+ etch stop. The understanding of how a planar layout is transferred into a three dimensional structure after the etching is essential in the design of hotplate. Some design guidelines will be given. Finally, we shall report the result of our EDP etching process.

### 3.1.2 Mechanism of Silicon Etch

A complete model of the silicon etch mechanism is given by H.Seidel [3.3] [3.4]. The overall reaction is summarized by the following reaction:

\[
\text{Si} + 2\text{OH}^- + 2\text{H}_2\text{O} \rightarrow \text{SiO}_2(\text{OH})_2^{2-} + 2\text{H}_2
\]  

(3.1)

Using this model, we can explain the high anisotropic (100)/(111) etch ratio and the dopant dependency. Basically, it is a redox reaction where the silicon is oxidized by the hydroxide ion. A complete breakdown of the reaction, which takes the \{100\} surface as an illustration, is given as follow.
After immersion of the wafer into the electrolyte, the Fermi levels of the solid/liquid interface align so that the bands in silicon bend downward. For \{100\} silicon surface atom, there are two (Si-Si) bond and two dangling bonds. The first reaction step involves the binding e\(^{-}\) from OH\(^{-}\) to one unpaired e\(^{-}\) to form an Si-O bond.

\[
\begin{array}{c}
\text{Si} \\
\text{Si}_{\circ}\text{Si}_{\circ} + \text{OH}^{-} \rightarrow \text{Si}_{\circ}\text{OH}
\end{array}
\]  \hspace{1cm} (3.2)

Since the \{100\} surface Si has two dangling bonds, two hydroxide ions are binded.

\[
\begin{array}{c}
\text{Si} \\
\text{Si}_{\circ}\text{OH} \hspace{1cm} + \text{OH}^{-} \rightarrow \text{Si}_{\circ}\text{Si}_{\circ}\text{OH}
\end{array}
\]  \hspace{1cm} (3.3)

The new Si-O bonds will weaken the backbonds of the surface atom because of the higher electro-negativity of oxygen atom than silicon atom. The next step is the breaking of the Si-Si backbonds. This corresponds to the thermal excitation of the binding electrons located at the orbitals B' into the conduction band.

\[
\begin{array}{c}
\text{Si} \\
\text{Si}_{\circ}\text{OH} \hspace{1cm} \rightarrow \hspace{1cm} \left[ \begin{array}{c}
\text{Si}_{\circ}\text{OH} \end{array} \right]^{2+} \\
\text{Si}_{\circ}\text{OH} \hspace{1cm} \text{Si}_{\circ}\text{OH}
\end{array} + 2e_{\text{cond}}^{-}
\]  \hspace{1cm} (3.4)

The energy difference between the (Si-Si) orbitals B' and the conduction band contributes significantly to the overall activation energy, especially in the KOH case. For EDP, the diffusion and solvation are the dominate effects. The silicon-hydroxide complex reacts further with two OH\(^{-}\) producing the orthosilicic acid.

\[
\begin{array}{c}
\text{Si} \\
\left[ \begin{array}{c}
\text{Si}_{\circ}\text{OH} \end{array} \right]^{2+} + 2\text{OH}^{-} \rightarrow \text{Si(OH)}_{4} + \text{Si}_{\text{solid}}
\end{array}
\]  \hspace{1cm} (3.5)

The neutral Si(OH)\(_4\) molecule will leave the solid surface by diffusion. Due to high pH value of the bulk electrolyte, the molecule is unstable and decomposes into a silicate complex and two protons.
\[ \text{Si(OH)}_4 \rightarrow \text{SiO}_2\text{(OH)}_2^{2-} + 2\text{H}^+ \] (3.6)

The excess electrons in the conduction band will be transferred to water molecules which are located near the solid surface, thus producing four hydroxide ions and hydrogen molecule.

\[ 4\text{H}_2\text{O} + 4\text{e}^- \rightarrow 4\text{OH}^- + 2\text{H}_2 \] (3.7)

Since the OH\(^-\) ions are supplied locally, the bulk OH\(^-\) concentration does not affect the reaction rate.

### 3.1.2.1 Etch Rate

One can increase the etch rate by increasing the temperature, according to the Arhenius law. On the \{100\} surface, the activation energy for EDP and KOH are about 0.40 eV and 0.6 eV respectively. Both reaction rates can also be increased by increasing the water content. Since diffusion plays a major role in EDP etch, simply stirring with inert gas can increase the etch rate. The stirring can also prevent oxygenation in air exposure which will darken the solution.

### 3.1.2.2 Role of Additives

The pyrocatechol in EDP system is used to increase the solubility of the etch product by converting Si(OH)$_4$ into a more complex anion.

\[ \text{Si(OH)}_4 + 2\text{OH}^- + 3\text{C}_6\text{H}_4\text{(OH)}_2 \rightarrow \text{Si(C}_6\text{H}_4\text{O}_2)_3^{2-} + 6\text{H}_2\text{O} \] (3.8)

Pyrazine acts as a catalyst. Its effect nearly saturates at a concentration of 3g pyrazine per liter ethylene-diamine. For the KOH system, the role of alcohol is mainly to adjust the relative water concentration without affecting the pH too much.

### 3.1.2.3 Residue

Residue always appears on the silicon surface after etching. The residue consists mainly of SiO$_2$ with additional trace amounts of reaction products. It is explained by the high dissolution rate of silicon atoms from the crystal surface as compared with the transport of the Si(OH)$_4$ complex into the bulk electrolyte. When the concentration of this complex
near the surface becomes too high, it will polymerize and result in the residue. For EDP solutions, the residue increases with the wafer content.

3.1.2.4 Anisotropic Behavior

The reaction sequence of \{111\} surface is identical to the above mentioned except for the fact that each \{111\} surface atom has only one dangling bonds and three backbonds. Therefore, three backbonds of the surface silicon atom have to be broken.

\[
\begin{align*}
\text{Si} & \quad \text{Si} - \text{OH} \rightarrow \text{Si} \left[ \text{Si} - \text{OH} \right]^{3+} + 3e_{\text{cond}}^{-} \\
\text{Si} & \quad \text{Si}
\end{align*}
\]  (3.9)

The corresponding orbital B' of the three backbonds configuration is expected to have a lower energy level than that of a \{100\} surface atom. The small difference of the backbond surface states energy accounts for the anisotropy. A small difference of 0.12 eV is sufficient to cause an etch rate ratio of 100:1 at room temperature. The relative etch rate of various silicon planes in EDP is illustrated in Figure 3.1.

3.1.2.5 Etching of Silicon Dioxide

The etching of silicon dioxide follows the chemical reaction

\[
\text{SiO}_2 + 2\text{OH}^- \rightarrow \text{SiO}_2(\text{OH})_2^{2-} 
\]  (3.10)

The etch rate is linearly proportional to the hydroxide concentration. The etch rate in KOH exceed those in EDP by about 100 to 1000 times. That is why silicon dioxide is considered to be the perfect masking for EDP etch. In order to use silicon dioxide in KOH system, low concentrated KOH must be used. This is because silicon etch rate increases with water content while silicon dioxide etch rate decreases with less OH\(^-\) ion. For example, the Si/SiO\(_2\) etch rate ratio can be as high as 1000 when using 15% KOH at 60°C. The etch rate of thermally grown oxide is approximately 30% lower than CVD oxide deposited at 800°C.
3.1.2.6 Boron Etch Stop

Silicon etch rate starts to decrease at a boron doping of approximately $2.3 \times 10^{19}$ cm$^{-3}$. The etch stop can be explained by the degeneracy of the boron-doped silicon. Boron-doped silicon starts to degenerate into metal when the doping level up to $2.2 \times 10^{19}$ cm$^{-3}$. The Fermi level will drop into the valence band, and the surface space charge layer will shrink to approximately one atomic layer. This means that the four electrons injected into the conduction band by the OH$^-$ oxidation step will have the probability of recombining with bulk holes. These recombined holes will not be available for the subsequent reaction with water molecules and cause a reduction of silicon dissolution. After degeneration, the number of surface e$^-$ available at the conduction band is inversely proportional to the hole and boron concentrations. The dissolution of one silicon atom require four electrons, the etch rate decrease with fourth power of boron concentration. The etch rate reduction is about 100 at boron doping $7 \times 10^{19}$ cm$^{-3}$.

3.1.3 Anisotropic Etching Patterns

A simple rectangular opening in the SiO$_2$ which x-y edges are aligned to $\{110\}$ silicon planes will result in the cross-section shown in Figure 3.2. At an intermediate stage, a pit with a flat bottom is formed. After a sufficiently long time, the etching stops under the very slow etch rate of $\{111\}$ planes. The sidewall has a 54.74° angle with respect to the silicon surface plane. The effect of misaligned rectangular open area is interesting. Figure 3.3 (a) and (b) shows some examples of such etching patterns. In general, the pit is the largest rectangle formed by these openings after a sufficient time in etching.

In case of several openings, if the pit regions meet during the etching, a larger pit will be defined by the smallest rectangle that encloses the openings. Figure 3.3 (c) and (d) gives two such examples. This characteristic is used to generate the suspended micro-hotplate by using four intersecting trapezoids like the one shown in Figure 3.3d.

3.1.4 Experimental Setup and Results

The EDP etch system is installed on a wet etch station (see Figure 3.4). The reflux system keep the solution concentration constant by condensing the evaporated solution. The
nitrogen purge keeps away oxygen which will oxidize the solution (turning red). The nitrogen is also used for stirring. The solution is heated by a hotplate whose temperature is controlled manually. We use fast etch rate composition since the residue is not a concern. The etching operates below boiling point (95-105°C) in order to minimize agitation of the wafer. Appendix C lists the detail procedure of the experiment. Suehle [3.5] added aluminum hydroxide Al(OH)₃ to the EDP solution to reduce the attack on any exposed aluminum pads. We found that in our experiment the Al etch rate is only reduced slightly. Even though Al remains after the etching, it is stained by the EDP. It is difficult to probe the pads afterwards. Worse yet Al₂O₃ precipitates at lower temperature (less than 50°C). Therefore, we did not use Al(OH)₃ but instead chose to overcoat the aluminum with a thin layer of gold to protect it from EDP etch. We shall discuss this in Chapter 4.

Table 3.2 summarizes the experimental results. The SiO₂ thickness is measured by Nanospec thin-film thickness measurement instrument. Silicon (100) etch depth is measured using both line width meter under microscope and Tencor Alpha Step instrument. Figure 3.5 illustrates the first method.

![Fig. 3.1](image.jpg)

Etch rates as a function of orientation on <100> wafer when using an EDP solution at a temperature of 95 °C (after [3.3]).
Fig. 3.2  Cross-section of a silicon substrate (a) before the etching, (b) at an intermediate stage and (c) after the etching has stopped.

Fig. 3.3  Top view of anisotropic etched examples. (a) and (b) have one opening while (c) and (d) has two and four openings. The thick solid lines are the opening boundaries. The dotted and narrow solid lines are the intersection of \{100\} etch stop planes. The shaded area are the suspended region. Pattern (a) results in a suspended corner and (b) result in a cantilever. Pattern (d) gives rise to the micro-hotplate structure.
Fig. 3.4  Diagram illustrating the experimental Setup of EDP etching in Microelectronic Fabrication Center Phase I wet etch station.

Table 3.2  Experimental data of EDP silicon etch.

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>Thickness of SiO₂ etched (Å)</th>
<th>Thickness of Si (100) etched (µm)†</th>
<th>Relative Si (100) etched rate (µm)</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>94</td>
<td>23.6</td>
<td>70.8</td>
<td>110°C, about 7150Å Al etched</td>
</tr>
<tr>
<td>40</td>
<td>149</td>
<td>40.8</td>
<td>51.6</td>
<td>102°C, with Al₂O₃ added (4g) and about 4320Å Al etched.</td>
</tr>
<tr>
<td>60</td>
<td>189</td>
<td>62.9 (56)</td>
<td>66.3 (56)</td>
<td>92°C, better N₂ purging, wafer face up.</td>
</tr>
<tr>
<td>90</td>
<td>-</td>
<td>53.7</td>
<td>53.7</td>
<td>92°C, better N₂ purging, wafer face down.</td>
</tr>
<tr>
<td>90</td>
<td>-</td>
<td>125</td>
<td>83</td>
<td></td>
</tr>
</tbody>
</table>

† Measured using line width meter under microscope. The bracket data is measured using Tencor Alpha Step.
3.2 Tin Dioxide Deposition

As discussed in Chapter 1, polycrystalline SnO₂ are used in the toxic gases detection. Gas sensor products based on thick film technology has been successful commercially over the last decade. For integrated gas sensor, a thin-film SnO₂ deposition process must be developed. The important factors of choosing the deposition process are:

i. Low temperature deposition

For process compatibility purpose, the substrate temperature should be kept below 150°C [3.6] if lift-off technique is used. Even though after the lift-off, the wafer temperature cannot be raised beyond 400°C because aluminum will melt. This requirement excludes the possibility of depositing pure tin and then oxidizes it at higher than 500°C.

ii. Control of oxygen content, grain size and porosity

The gas sensitivity depends on the oxygen content because sensing mechanism is based on the surface reaction between the chemisorbed oxygen and the reducing gases. For maximum sensitivity or modulation of selectivity, the oxygen content has to be optimized. The sensitivity increases rapidly with smaller grain size [3.7] as the reaction only occurs at the grain surface boundary. Therefore, small grain size and high porosity are highly desired.
Table 3.3  Deposition condition and result thickness of tin dioxide reactive sputtering.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Substrate temperature (°C)</th>
<th>Ar : O₂</th>
<th>Vacuum Pressure (mTorr)</th>
<th>R.F gun power (W)</th>
<th>Time (sec)</th>
<th>Film thickness (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>150</td>
<td>5:1</td>
<td>40</td>
<td>300</td>
<td>2000</td>
<td>5200</td>
</tr>
<tr>
<td>2</td>
<td>120</td>
<td>5:1</td>
<td>40</td>
<td>300</td>
<td>400</td>
<td>890†</td>
</tr>
</tbody>
</table>

† The film uniformity is ±9.6%.

iii. Ability of doping

Introducing thin layer of catalyst\(^1\) on top or in situ doping can modulate the selectivity. For example, doping of Pd [3.9] and Al [3.10] can increase the sensitivity towards ethanol and NO\(_\text{x}\).

In this work, we used RF power reactive sputtering of pure tin in oxygen ambient to deposit tin oxide at low temperature. We used the Denton Sputtering System (Model SJ/24LL). It is a multi-target sputtering system. The best vacuum that it can operate is \(4 \times 10^{-7}\) Torr. The three sputtering guns can operate simultaneously so that in situ doping is possible. It has a 4” substrate holder, residual gas analyzer, substrate heating and loadlock. Table 3.3 summarizes the deposition condition and result.

The deposited film is characterized by the oxygen content and grain size. From the X-ray Photoelectron Spectroscopy (XPS) result, the oxygen content of the second sample is about 41%. The sample deposited under high vacuum is very pure as shown in the XPS result (Figure 3.6). The oxygen content can be increased by thermal annealing in oxygen ambient after lift-off. As the grain structure affects the gas sensitivity, we studied the tin dioxide surface with Scanning Tunneling Microscopy (STM). Figure 3.7 shows the STM photos of the two samples. The first sample gives a nice grain structure while the second does not. The higher substrate temperature during the deposition favors the crystal growth.

\(^1\) The catalyst promotes the surface absorption of certain gases.
Fig. 3.6  X-ray Photoelectron Spectroscopy analysis of the second tin dioxide sample. The top graph records the emission of electron in orbital 3d3 and 3d5 of tin. The bottom graph records the emission of electron in orbital 1s. The sharp peaks and low background emission in the graph indicate that the sample is very pure. Other than tin and oxygen, the analysis only detects less than 0.1% of carbon.
Fig. 3.7  STM photos of deposited tin dioxide film. The first sample (top) shows a well-aligned rectangular grain structure. The grain size is about 250 × 400 nm. The second sample (bottom) does not show sharp grain boundary but still regular patterns can be clearly seen. Please refer to Table 3.3 for deposition conditions.
Table 3.4  Explanation of the IGS003 mask layers.

<table>
<thead>
<tr>
<th>Alignment sequence</th>
<th>Layer name</th>
<th>Bright field</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st</td>
<td>pdiff</td>
<td>N</td>
<td>P+ diffusion</td>
</tr>
<tr>
<td>2nd</td>
<td>contact</td>
<td>N</td>
<td>P+ to metal contact</td>
</tr>
<tr>
<td>3rd</td>
<td>metal</td>
<td>Y</td>
<td>Metal routing</td>
</tr>
<tr>
<td>4th</td>
<td>pad</td>
<td>N</td>
<td>Pad opening and metal to sensor contact</td>
</tr>
<tr>
<td>5th</td>
<td>sensor</td>
<td>N</td>
<td>Sensor patterned by lift-off</td>
</tr>
</tbody>
</table>

3.3 Design Layout

In this thesis, two sets of masks (IGS002 and IGS003) are designed, and they are written using the *E-beam machine* at Standford University and the *Laser Direct Write Machine* from Intertech respectively. Prototype devices have been successfully fabricated using IGS002 masks. On the basis of the result and experience with IGS002 masks, the author redesigned a new set of structures in IGS003. In this section we shall describe only the IGS003. Some test patterns which are specifically designed to monitor the integrated gas sensor process will also be discussed.

The design was drawn using Cadence's Virtuoso Layout Editor. There are six drawing layers and five mask layers. Table 3.4 explains the mask layers. The extra drawing layer called *open* will be converted into *contact* and *pad* layers. The die size is 5 × 5.3 mm. The complete die layout is shown in Figure 3.8. The mask set contains 186 sensor dies. Each die contains 17 sensors and a few structures for stress analysis. Table 3.5 explains the purpose of each sensor cell. The dimensions of the bridges for S-01 and S-03 to S-10 are listed in Table 3.6.

---

2 The stress analysis test structure are designed for another project. However, the analysis is also useful to study the mechanical property of the sensor structures.
Fig. 3.8  A complete layout of the sensor die in IGS003 masks. Each sensor cell is labelled with a mnemonic on the die. Table 3.5 explains the purpose of each sensor cell.
Table 3.5: Legends for the sensor cells in IGS003 layout.

<table>
<thead>
<tr>
<th>Mnemonic</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>S-OLD</td>
<td>the old sensor using 3 micron design rule in IGS002 layout.</td>
</tr>
<tr>
<td>S-01</td>
<td>the default sensor.</td>
</tr>
<tr>
<td>S-02</td>
<td>the improved version of S-OLD without modifying the basic design.</td>
</tr>
<tr>
<td>S-03 to S-05</td>
<td>the default sensor with different bridge lengths.</td>
</tr>
<tr>
<td>S-06 to S-08</td>
<td>the default sensor with different metal line width.</td>
</tr>
<tr>
<td>S-09 to S-10</td>
<td>the default sensor with different bridge width.</td>
</tr>
<tr>
<td>S-11</td>
<td>intended for using sensing film etching instead of lift-off (i.e. bright</td>
</tr>
<tr>
<td></td>
<td>field pattern by inverting image in dark field mask).</td>
</tr>
<tr>
<td>S-12</td>
<td>using 4 points method to measure sheet resistance of sensor film.</td>
</tr>
<tr>
<td>S-13</td>
<td>using aluminum plate together with 4 point method to sense the</td>
</tr>
<tr>
<td></td>
<td>active area temperature.</td>
</tr>
<tr>
<td>S-14</td>
<td>with the heater at edge of bridge extended.</td>
</tr>
<tr>
<td>S-15</td>
<td>with the heater stretched inward.</td>
</tr>
<tr>
<td>S-16</td>
<td>the magnified (2×) version of the default sensor to test the scaling of</td>
</tr>
<tr>
<td></td>
<td>the micro-hotplate.</td>
</tr>
<tr>
<td>ARR1</td>
<td>array of four S-01.</td>
</tr>
<tr>
<td>ARR2</td>
<td>array of four S-01. It allows different sensing film on each element</td>
</tr>
<tr>
<td></td>
<td>with the help of array alignment mark (refer to 3.3.3.3).</td>
</tr>
</tbody>
</table>

Table 3.6: Dimension of the bridges for S-01 and S-03 to S-10.

<table>
<thead>
<tr>
<th>Sensor</th>
<th>S-01</th>
<th>S-03</th>
<th>S-04</th>
<th>S-05</th>
<th>S-06</th>
<th>S-07</th>
<th>S-08</th>
<th>S-09</th>
<th>S-10</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bridge Width (µm)</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>30</td>
<td>24</td>
<td>37</td>
</tr>
<tr>
<td>Bridge Length (µm)</td>
<td>75</td>
<td>50</td>
<td>62</td>
<td>88</td>
<td>101</td>
<td>75</td>
<td>75</td>
<td>75</td>
<td>75</td>
</tr>
<tr>
<td>Metal Width (µm)</td>
<td>5.00</td>
<td>5.00</td>
<td>5.00</td>
<td>5.00</td>
<td>5.00</td>
<td>3.54</td>
<td>6.36</td>
<td>5.00</td>
<td>5.00</td>
</tr>
<tr>
<td>Metal Length (µm)</td>
<td>68</td>
<td>43</td>
<td>55</td>
<td>81</td>
<td>94</td>
<td>68</td>
<td>68</td>
<td>68</td>
<td>68</td>
</tr>
</tbody>
</table>
Fig. 3.9  Test pattern to characterize the silicon etch.

Fig. 3.10  Test pattern to measure the sheet resistance of P+ under the suspended plate.

Fig. 3.11  Alignment mark for the alignment of different sensor films on an array sensor.
All the test patterns are included in one die, and there are 25 such dies in the masks. We shall only cover the test patterns specific for the integrated gas sensor process. Figure 3.9 shows the test patterns for silicon etch characterization. The five squares measure the silicon \{100\} etch rate using the line width method described before. The blossom pattern [3.3] measures the relative etch rate of different silicon planes. After etching, it will give a pattern similar to Figure 3.1. Since the EDP etch only stop at highly doped P+ region, the P+ resistor under the micro-hotplate is thinner and has a higher resistance. The test pattern shown in Figure 3.10 measures the etched P+ sheet resistance using 4-point probe method.

The array sensor alignment mark shown in Figure 3.11 enables the patterning of four thin-films in the sensor array using one sensor mask layer. Normally, the bigger \(\square\) on sensor mask is aligned to the smaller \(\square\) with label “BL” on the wafer. If we want to pattern the top-left sensor, the bigger \(\square\) on sensor mask is aligned to the smaller \(\square\) with label “TL” on the wafer. The procedure is similar for the alignment of top-right and bottom-right sensor.

### 3.4 Conclusion

In this chapter we have described the anisotropic silicon etch, tin oxide deposition process and the design of IGS003 test chip. Ethylene-diamine Pyrocatechol solution is chosen to etch the silicon because of its negligible etch rate of silicon dioxide. The theory that explains the anisotropy etching and doping concentration dependency of the etching was also discussed. An experimental setup of the silicon etch was developed, and the results showed an etch rate of about 70 \(\mu\)m/hr. The Denton Sputtering System (Model SJ/24LL) was used to deposit the tin oxide. The deposited film contained 41 % oxygen, and it is very pure. Finally, the design of IGS003 integrated gas sensor test chip was described. The design included 17 sensor cells with variations of bridge dimensions. Several test patterns designed to characterize the etching process. A novel technique to create sensor array with each element having a different sensing film is reported.
3.5 Reference


Chapter 4

Micro-hotplate Technology

Micro-hotplate (MHP) is a new terminology in microelectronics era. This term was firstly used by Suehle [4.1] to define a thermally insulated platform fabricated using microelectronics technology. It plays an important role in the realization of \(^1\)integrated gas sensor. MHP heats up the sensing material so that the device can operate at maximum sensitivity. It is also important for the MHP to have uniform temperature. The ease of fabrication is important in terms of manufacturability. It is less risky if the fabrication is compatible with standard microelectronics technology such as CMOS or bipolar. The first MHP for thin-film gas sensor was reported by Wise [4.2]. The structure was adopted from pressure sensor. Figure 4.1 shows the cross-section of the structure.

However, this approach uses backside anisotropic etching of silicon to form the thermally insulated structure. The backside processing steps make it incompatible with conventional integrated processing technology. It is desirable that the fabrication process is compatible with standard processing with minimal changes.

\(^1\) The usage of the term integrated is very controversial. In a more strict sense, it describes a process or structure that can be easily integrated with conventional electronic circuit. People usually use it for a structure that is fabricated by microelectronic technology. In this work, we refer the term integrated to the former.
1) Double side P+ diffusion, dielectric and metal definitions

![Diagram of double side P+ diffusion, dielectric and metal definitions]

2) Thin film sensing material definition, EDP etch

![Diagram of thin film sensing material definition, EDP etch]

**Fig. 4.1** One example of MHP fabricated with backside etching. The etching begins at backside and terminates at masking material at the front. Because of the limiting accuracy in the backside alignment, P+ rim is usually added.

The MHP structures have not changed much up to 1993, when Suehle reported a micro-hotplate for gas sensor using commercial CMOS foundry fabrication and additional post-fabrication processing [4.1] (Figure 4.2). The conventional backside process is replaced by frontside etching together with proper layout. The structure was originally designed for dynamic thermal scene simulation [4.3]. They converted it into a thin-film gas sensor by the deposition of tin dioxide on packaged die. Base on a similar approach, we report a novel MHP structure with improved thermal management -- better temperature uniformity and temperature sensing. The fabrication process is significantly simplified without loss of performance. In this chapter, the design, fabrication and characterization of the MHP are presented.

### 4.1 Device design

The attributes of an optimal MHP for thin film gas sensor are:

1. Good thermal isolation between MHP and bulk (larger than 1.5°C/mW as discussed in Chapter 3).
2. Good temperature uniformity within the active area (less than 30°C).
3. Fast thermal response time.
4. Ability to sense the active area temperature.
5. Minimum additional steps and masks compared to conventional fabrication technology.

With this in mind, we proposed a new MHP design. Table 4.1 compares the two designs.

### 4.1.1 Device structure

Figure 4.3a shows the cross-section of the proposed MHP. We choose to use boron doped diffusion to provide both the heating and temperature sensing function. For temperature sensing, P+ diffusion is better than aluminum and polysilicon. Aluminum has very low resistivity and temperature coefficient resistance (TCR) for a temperature sensor. Four-point probe method must be used to measure the resistance. P+ diffusion has a higher TCR than aluminum, and a simple two-terminal resistor can be used as temperature sensor. The temperature characteristic of polysilicon depends very much on the process conditions such as dopant dose, deposition temperature, and annealing temperature and time [4.4]. On the contrary, TCR of P+ diffusion depends solely on doping, and the characteristic is well known. The TCR changes from positive to negative as the doping increases. One more advantage of P+ diffusion is that it does not induce any surface profile. It helps to achieve a more planar final surface profile for thin-film deposition.

As pointed out in Table 4.1, our suspended structure is thinner than Suehle's design. Thinner does not mean a weaker mechanical support because thicker plate is heavier. Interestingly, this thin plate can blend to some extent without fracture as will be discussed later. The reason is that the bridges are supported by the aluminum and the CVD oxides while the former is elastic. Mechanical stress analysis can be applied to analyse the mechanical stability of the micro-structure. Besides, it is expected that the thinner plate has faster thermal response because of smaller thermal mass. This will be confirmed by measurement later.
Fig. 4.2  Suehle's micro-hotplate structure: (a) cross-section, (b) layout without showing the second metal layer and second dielectric layer.
Fig. 4.3 Proposed micro-hotplate structure in this thesis: (a) cross-section, (b) layout design showing all the five layers.
Table 4.1 A direct comparison between MHPs proposed by Suehle and the author.

<table>
<thead>
<tr>
<th>Feature</th>
<th>Suehle’s MHP</th>
<th>Proposed MHP</th>
<th>Comment</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fabrication Process</strong></td>
<td>CMOS Foundry Process</td>
<td>Compatible to standard process, single layer metal, no poly and field oxide</td>
<td>Only subset of standard processes is used to simplify the fabrication. It is also easier to analyze the simpler structure</td>
</tr>
<tr>
<td><strong>Heater Structure</strong></td>
<td>Poly heater serpentine</td>
<td>P+ diffusion heater in a guard heater arrangement</td>
<td>Température distribution improved</td>
</tr>
<tr>
<td><strong>Temperature Sensing</strong></td>
<td>Aluminum plate with 4-point van de Pauw measurement</td>
<td>P+ diffusion resistor just under the active area</td>
<td>Pin counts reduced by two, the Al plate measures the average temp. of hotplate but not active area</td>
</tr>
<tr>
<td><strong>Supporting Material</strong></td>
<td>2nd CVD / 2nd Al / 1st CVD / 1st Al / field oxide</td>
<td>2nd CVD / Al / 1st CVD</td>
<td>Supporting bridges are much thinner but it does not mean a weaker mechanical support. It is because the first MHP is heavier</td>
</tr>
<tr>
<td><strong>Thermal Response</strong></td>
<td>Expected to be faster</td>
<td></td>
<td>The thermal mass of the first MHP is larger</td>
</tr>
<tr>
<td><strong>Topology</strong></td>
<td>Non-planar due to double metal and poly</td>
<td>More planar due to single metal and no poly</td>
<td>Good surface planarity is essential for thin film deposition of the sensor.</td>
</tr>
<tr>
<td><strong>Sensing Film Formation</strong></td>
<td>Deposit on packaged and EDP etched chip without any lithography</td>
<td>Deposit and pattern by lift-off before packaging and EDP etch</td>
<td>Array of sensors with different materials cannot be implemented in the first MHP</td>
</tr>
</tbody>
</table>
Other than acting as the electrodes to both the sensing thin film and the diffusion resistor underneath, the aluminum provides a low thermal resistance plate to disperse the heat generated. Aluminum has much higher thermal conductivity than oxide (about 170 times). The structure is analogous to a domestic hotplate. The heat generated at the bottom P+ heater is dispersed by the sandwiched Al layer which in turn heats up the sensing film at the top.

4.1.2 Layout design

Figure 4.3b shows the layout of the micro-hotplate design that is drawn using an integrated circuit layout editor from CADENCE. The abstract drawing layer open, which exposes the silicon surface for etching, is converted into contact and pad opening layers before the final translation into physical layout file. The design rule check commands in CADENCE to do this are

```plaintext
pad = geomOr("pad", "open")
contact = geomOr("contact", "open")
```

If CMOS process is used, the whole MHP should be enclosed by active area to get rid of the field oxide. Etching from the four open trapezoids gives rise to the suspended structure [4.5]. The etching process can be described as follows. Etching starts from the four trapezoids. Rectangle pit are etched in the beginning. When two such etched pits meet, the etching rate increases at the convex corners. Eventually, the silicon below the plate will be etched away.

To maintain uniform temperature across the sensing film, the guard heater concept [4.6] is adopted in our MHP design. The idea is that the heater should guard the heat dissipation from the active area to the bulk so that there is no heat flow on the active area. According to the law of heat conduction (Equation 4.1), there will be temperature difference if there is heat flow.

\[ q = -kA \frac{dT}{dx} \]  

[4.1]
Fig. 4.4 Illustration of the use of guard heater in one dimensional case. (a) Uniform heating will result in large temperature variation on active area. (b) For guard heater arrangement, a point heat supply is applied at the edge of active area and gives uniform temperature on active area.

where \( q \), \( k \) and \( A \) are the heat flux, thermal conductivity and cross-sectional area. For one-dimensional case (Figure 4.4 a), the guard heater is a point heat source at the edge of active area. For the real MHP problem that is two-dimensional, we want heat dissipation starting at the edge of each bridge. Therefore, the heaters are placed at the edges of the bridge (Figure 4.5). *Any other heating inside the hotplate will create hot spot because the dissipation path is already guarded.*

The P+ temperature sensor is placed under the active area, and therefore it senses the average temperature of the active area. It will be shown later that the thermal resistance of the hotplate is roughly equal to thermal resistance of the four bridge metal lines. Hence the thermal resistance between active area and substrate \( \theta_{os} \) is

\[
\theta_{os} = \frac{L}{4k_A A} \tag{4.2}
\]
where $k_{Al}$ is the thermal conductivity of aluminum, $L$ is the length of bridge and $A$ is the cross-sectional area of aluminum. This means wider metal line will require longer bridges for the same thermal resistance. Therefore, the metal line width and bridge length should provide a tradeoff between current density, thermal resistance and mechanical stability of the structure. The hotplate is filled with aluminum whenever possible to disperse the heat generated. Finally, a P+ diffusion guard ring surrounding the suspended area is added to prevent too much undercut at the periphery caused by the finite etch rate of silicon $\{111\}$ plane. This will be discussed in section 4.5.

4.1.3 Simulation

Thermal simulation using finite element analysis programs PATRAN and ABAQUS has been described in previous chapter. The same methodology is applied to simulate the thermal characteristics of the micro-hotplate. The simulation here is more precise than those described in Chapter 2. The solid model includes all the layers (1st and 2nd CVD oxide, aluminum, P+ diffusion and silicon). The model retains the routing of metal and diffusion as much as possible. It also includes the temperature dependence of material thermal conductivities while ignoring the effect of convection and radiation. The ambient temperature is 50 °C and the package thermal resistance is 110 °C/W. From the simulation, the power is 30 mW at an operating temperature of 350 °C.
The maximum temperature difference across the active area is about 25 °C. The substrate surface temperature drops very rapidly near the bridge ends. It is well below 51 °C at a distance of 100 µm from the bridge ends. The simulated temperature contour is shown in Figure 4.6. The contour appears asymmetrical in the horizontal direction. This is due to the imbalance of both the heat supply from the P+ heater and the heat dissipation along the bridge metal lines at left and right hand sides. By redesigning the layout to make the heat supply and heat dissipation more symmetrical, lower heating power and better temperature uniformity can be achieved. This will be discussed in a later section.

4.2 Fabrication

Figure 4.7 shows the processing sequence of the integrated thin-film gas sensor. The fabrication process begins with (100)-oriented 4-7 Ω-cm n-type wafers. A boron diffusion defines the resistive heater, temperature sensor, and the etch stop rim. 0.8 µm CVD oxide is deposited as the first dielectric layer. Contacts are patterned to define P+ contacts and opening area. Next, a stack of Gold/Titanium-Tungsten/Aluminum (Au/Ti-W/Al) is sputtered and patterned to form the interconnection. Gold is used to protect any exposed aluminum from EDP attack. Meanwhile, Ti-W provides the adhesion layer between the two metals. 0.7 µm phosphorus doped glass (PSG) are then deposited as the second dielectric layer. The PSG is in compressive stress and compensates the tensile stress induced by the first oxide layer. Pads, sensor film contacts and the opening area are then defined. The silicon etch must follows the last step that requires lithography. It will be very difficult to perform the lithography after the silicon etch. The resist on the suspended plate will have uneven thickness. The plate also bows down slightly. The exposed pattern on it will then be blurred due to the small field of depth of the contact aligner. Although some lithography techniques such as ion milling method [4.7] developed recently can transfer pattern to highly non-planar substrates, the method is very cumbersome.
Fig. 4.6  A color temperature contour of the micro-hotplate, plotted by PATRAN. The meshing grid lines are shown as well. The operating temperature is 350°C.
Fig. 4.7  Process flow of a micro-hotplate structure. The silicon etch is either before or after the packaging.
Method A

Silicon etch

Package

Tin oxide (w/o lithography)

Method B

Tin oxide (w/ lithography)

Silicon etch

Package

Fig. 4.8 Two alternative process flows after pad definition. The silicon etch is not necessary before packaging (will be discussed later).

There are two ways to solve the problem as shown in Figure 4.8. Method A, which is used by Suehle, performs the tin oxide deposition after the packaging and silicon etch. The tin oxide is left un-patterned. It utilizes the fact that tin dioxide is effectively an insulator at room temperature. The drawbacks are awkward processing sequence and leakage caused by the poor insulating property of SnO2. It also sacrifices the advantage of batch process. Interestingly, this method allows each chip to have a different thin-film.

Method B performs the deposition and patterning of tin oxide before the etching and packaging. This method allows batch processing and patterning of the tin oxide. It must be used for the implementation of array sensor. We have tested the etch resistance of tin oxide in EDP. For two hours in EDP, no sign of etching is observed. This may not be true for other gas sensing material such as TiO2. In case the EDP attacks the thin-film, a thin sacrificial oxide layer can be used to protect the thin-film. Both methods have been tried in our study.

Silicon is etched in an Ethylenediamine-Pyrocatechol (EDP) etching system [4.8] for about two hours to form the micro-hotplate pit. A fast etching composition is used because the amount of residue is not important. It is not necessary to etch up to the point
that the \{111\} planes meets. The etching can be stopped when the whole plate is suspended. The required etch time is difficult to calculate based on the etch rate. In fact, the end point can be observed under microscope because the thin oxides are transparent.

The P+ doping must be higher than $7 \times 10^{19}$ cm$^{-3}$ to effectively stop the EDP etch [4.9]. This doping can be achieved using PMOS source/drain diffusion in a CMOS process or the emitter diffusion of PNP in a bipolar process. In this work, the doping is obtained by long duration boron disk diffusion. Implantation cannot provide a high surface concentration, unless Rapid Thermal Process is used for anneal. Alternatively, a combination of shorter boron disc diffusion and implantation can also do the job. Figure 4.9 shows the process simulation results of the two approaches.

Special attention must be paid to the packaging of the sensor chip. The normal die separation has a very harsh environment for the microstructure to survive. It is not unusually to have 100 psi water jet during the cutting. For this purpose, the water jet should be replaced by low pressure rinse after dicing. The wafer can be coated with photo-resist to prevent debris resulted from cutting. An alternate approach is to etch the packaged chip rather than wafer.

Figure 4.10 shows the SEM photographs of a MHP structure fabricated using the IGS002 mask set. The metal leads are clearly shown. Hillocks on aluminum appear because of the high temperature LPCVD step (~400 °C). The plate bows downward because of the gravitational force. The structure can be observed more clearly from the microscope photos as the thin oxides are transparent. Figure 4.11 shows the structure in the midst and at the end of etching. A close-up in Figure 4.12a clearly shows the P+ diffusion resistor. Figure 4.12b shows the MHP that uses Al plate to sense the temperature and is designed using 5μm design rule. Figure 4.13 shows an array of four sensors.
Fig. 4.9  Doping profiles of (a) long boron diffusion and (b) combination of shorter boron diffusion and implantation, simulated by SUPREM IV.
Fig. 4.10  SEM photograph of a micro-hotplate structure after EDP etching. The hotplate area is $136 \times 120 \ \mu m^2$ and the active area is $60 \times 50 \ \mu m^2$. The sample does not have tin oxide deposited. The plate bows down slightly.
Fig. 4.11  Microscope photos of the micro-hotplate structures (a) in the midst of etching and (b) at the end of etching.
Fig. 4.12 Microscope photos of the micro-hotplate structures. (a) shows a close up of the plate. (b) shows a MHP using aluminum plate to sense the temperature. Since 4-point probe method is used, the number of metal leads becomes 8.
Fig. 4.13  Microscope photo of an array of micro-hotplate structures.

4.3 Heater Characterization

Active area temperature and the heater power were measured. The measurement was done on wafer using a Wentworth wafer probe station MP-900 with Wentworth hot chunk TC-100. The devices were heated from room temperature to about 320°C, and the temperature sensor resistance ($R_s$) is measured. This gives the calibration curve of $R_s$ versus temperature (Figure 4.14). Next constant current is applied to the heater, and the $R_s$ values are recorded. The temperature of the active area $T_O$ is then derived from the previous calibration curve. The heater power ($P_h$) is obtained by multiplying the current by the voltage across the heater. Figure 4.15 shows the graph $T_O$ against $P_h$. Due to the decrease of thermal conductivity at increasing temperature, the heating efficiency increases with temperature.
Fig. 4.14  Temperature sensor resistance ($R_s$) versus hot chunk temperature. The whole wafer is held at constant temperature by the hot chunk.

Fig. 4.15  Hotplate active area temperature versus heater power. The ambient temperature is 45 °C. The dotted straight line ($7.02 P + 45$) is included as a reference.
The best quadratic fit of the calibration curve is \( 0.14 P^2 + 7.02 P \), where \( P \) is the heater power in mW. The linear coefficient can be interpreted as the heating efficiency or thermal resistance \( \theta_{OS} \). Using Equation 4.2, the calculated effective thermal resistance of the four bridge metal lines is 7.27 °C/mW. This is in good agreement with the measured heating efficiency (7.02 °C/mW).

### 4.4 Limitations

During the experiment, it is found that the aluminum near the top, bottom and right side melts when the active area is about 300°C. Figure 4.16 shows a photo of the burned out MHP. After the melting, the device is ruined. The operating temperature of tin dioxide is around 350°C. Therefore, the device will have difficulty in working at the high end of the temperature range. The fact that aluminum melts at about 500 °C indicates the existence of severe overheating on the hotplate. As explained in Chapter two, the heat dissipation is guarded at the bridges. Any heat generated inside the hotplate will accumulate and form the hot spot. Actually, the burned region as seen in Figure 4.16 coincides with the hot spot in the simulated contour shown in Figure 4.6. We have overlooked the consequence of the hot spot during the first layout design. Another limitation is the unbalance of heat dissipation as discussed in section 4.1.3. The left bridges have a smaller thermal resistance than the right ones. This causes a net heat flux flowing from right to left. The heat flux degrades the temperature uniformity and also over heats the right side of the hotplate.

The problems can be alleviated by proper change of the layout. Firstly, any unnecessary heating inside the guard heaters should be eliminated. Secondly, the heat dissipation path should be symmetrical in both horizontal and vertical directions. The argument is verified by the simulation of a modified version of the previous model. The heating effect of the P+ resistor between the guard heaters are turned off. The width of aluminum lines at each bridge is made equal in order to balance the heat dissipation. Figure 4.17 shows the simulated temperature contour. The heat accumulation is reduced significantly and the temperature uniformity is also improved. The second mask design is intended to alleviate the problems.
Fig. 4.16 The microscope photo of a burned out MHP. The burned region agrees very well with the thermal simulation.

significantly and the temperature uniformity is also improved. The second mask design is intended to alleviate the problems.

The first problem can also be solved by using higher melting point metal such as gold or tungsten as the routing material. However, these metals are not compatible with standard CMOS technology and are more expensive than aluminum. Aluminum also has the advantages of low density and high yield strength. Besides, note that perfect symmetry is difficult to achieve in the fabricated device because of alignment errors. We have to look for other solutions for the second problem.
Fig. 4.17 The temperature contour of a modified MHP. The heating effect of the P+ resistor between the guard heaters are turned off. The width of aluminum lines at each bridge is equalized to balance the heat dissipation.
Fig. 4.18  The temperature contour of a MHP with heating applied to the center temperature sensor at the same time. The hot spot temperature is lower and the temperature uniformity remains more or less the same.
Another approach is to apply heat to the center temperature sensor at the same time. The idea is to make the center hotter than the periphery. However, if one is not careful, the temperature uniformity will be degraded. The approach is verified with simulation as shown in Figure 4.18. The hot spot temperature is lower and the temperature uniformity remains more or less the same. The approach has also been verified by experiment. We applied $1/8$ of the heater power to the P+ temperature sensor. The same measurement was carried out and the MHP temperature could rise beyond $350^\circ$ C without burning. However, one difficulty in applying the two-heater approach is to determine the second heater power. It has to be determined experimentally because the asymmetry caused by alignment errors varies for different wafers. It is possible only if microscopic surface temperature measurement can be made. We do not have this capability. We shall rely on the simulation to tune the second heater power.

4.5 Modified Design

In the new design, only the sensor layout is modified. The basic structure and the process remains unchanged. Figure 4.19a compares the new design and the old design. The major changes incorporated are:

1) **Removal of unnecessary heating**: the P+ links between adjacent guard heaters cause the hot spots. They are splitted and connected by metal link.

2) **Balance of heat dissipation**: two dummy aluminum lines are added onto the left bridges so that the bridge metal lines are symmetrical. Inside the hotplate, the metal plate are placed as symmetrical as possible.

3) **Better mechanical support**: the anchors at the bridge ends are strengthened in the layout. The bridge length is also shortened.

Figure 4.19b shows the new design. The layout has been implemented in masks set IGS003.
Fig. 4.19 (a) illustrates several ways to improve the temperature uniformity, heat accumulation problem and mechanical stability from the old design. (b) shows the layout of the modified design.
4.6 Conclusion

We have described the design and fabrication of a novel micro-hotplate structure. The process is compatible with standard integrated processing technology by avoiding the uses of backside etching and auxiliary metal. The fabrication process is much simpler than the previous reported structure. Sensing film patterning is supported and exposed aluminum is protected by gold overcoating. The use of P+ diffusion improves temperature sensing and surface profile. The device is successfully fabricated and exhibits high heating efficiency. The use of guard heater design improves the temperature uniformity. This is verified by finite element simulation.

During the characterization of the heater, we discovered that the hotplate has over-heating problem. The aluminum melted at a temperature lower than expected. The problem can be eliminated by using two-heater approach or better layout design. The two-heater solution was verified both by simulation and by experimental measurement. The heat accumulation was significantly reduced. Meanwhile, we faced the problem of how to determine the power applied to the second heater. The only solution at this stage is to rely on thermal simulation.

Finally, the layout design is modified to correct the over-heating problem, improve the temperature uniformity and also improve the mechanical stability. The new design is incorporated into masks set IGS003. The micro-hotplate developed will be an excellent platform for the on-going research in integrated thin film gas sensor.

4.7 Reference


Chapter 5

Summary and Suggestions for Future Work

5.1 Summary

The thesis focused on three main areas as summarized in the following.

5.1.1 Thermal Analysis

The application of finite element analysis to simulate the thermal behavior of micro-hotplate structure was investigated. The MCAE softwares PATRAN and ABAQUS were used. The analysis can estimate the temperature distribution, heater power and also allow empirical modeling of thermal resistances. Four published structures were analysed and compared.

5.1.2 Process Development

1. The anisotropic silicon etch process using Ethylene-diamine Pyrocatechol solution was developed. The experimental setup and result data were presented. The etch rate was determined to be about 70 μm/hr.

2. Low temperature thin-film tin oxide was deposited using R. F. reactive sputtering of tin target under oxygen amibent. Preliminary characterization result shows that the film has a regular grain structure, and the oxygen content is about 40%.
3. Two mask sets IGS002 and IGS003 were designed. IGS003 is an improved version of IGS002. In IGS003, various sensors are drawn to study the effect of bridge dimensions and scaling etc. Specialized test patterns are designed for the process.

5.1.3 Micro-hotplate Technology

1. A novel MHP structure was proposed to improve Suehle's design for better thermal management. The fabrication process is simple and compatible with standard integrated processing technology. The device has the advantages of better temperature uniformity, better temperature sensing, better surface profile and support of sensing film patterning.

2. Thermal analysis was used to simulate the design. It was useful in estimating the thermal resistance of the hotplate, verifying the temperature uniformity and the resolving the over-heating problem described in Chapter 4.

3. The hotplate was characterized and the heating efficiency was found to be 7°C/mW. During the characterization, the over-heating problem on the hotplate was discovered. We suggested to redesign the layout or use a two-heater approach to alleviate the problem. The layout modification was implemented in the second set of masks, IGS003.

5.2 Suggestions for Future Work

The work associated with the MHP design and fabrication is almost complete except the surface temperature measurement. The author strongly encourages the future researchers to use the developed MHP as the platform for the investigation of gas sensor characteristic. Many research directions are identified and discussed below.

5.2.1 Surface Temperature Measurement

Surface temperature measurement technology is the most fundamental for investigating the thermal performance of a MHP. It is very important to verify the simulation result by the
measurement. The technique also helps to check the quality of the hotplate. As mentioned in Section 4.4, the over-heat problem can be alleviated by using two-heater approach. If the surface temperature can be measured, one can tune the second heater power easily.

Several kinds of techniques have been reported for measuring the surface temperatures of ICs [5.1]. The techniques are generally classified into electrical method (EM), and infrared microscopy (IRM) [5.2] and liquid crystal thermography (LCT) [5.3]. Electrical method uses diode as a temperature sensor. Although the technique is very accurate, the incorporation of a diode may affect the temperature distribution and the fabrication process. It is also not easy to provide the thermal image. The IRM method is so far the most convenient one to obtain temperature profile. Computerized IRMs are commercially available. One serious drawback is its low spatial resolution (15 μm). We can only have an image of 9×8 pixels for an hotplate area of 136×120 μm².

The most promising technique for our application is LCT. Some liquid crystals change their colors at different temperature. However, the temperature range for the color change is usually too small for temperature measurement. Some other liquid crystals change from nematic state into isotropic state [5.4] at a very sharp transition temperature (~0.1°C). If a polarized light source is applied, the film will turn from transparent to opaque. This kind of temperature measurement is called a "transition point technique". This technique has been routinely used in IC industry for locating leakages or defects. The spatial resolution is only limited by the optical microscope resolution. The method is also inexpensive as compared with IRM. Merck House, England is one of the LC vendor. A complete system for LCT is available from Tempronic Corporation, US.

We cannot directly obtain the temperature profile using the LCT technique. Usually the maximum transition temperature provided from the vendor is not higher than 200°C. The boundary of the dark area is the contour at the transition temperature. By varying the heating power, many pictures can be taken to estimate the temperature profile. The exact temperature profile may not be available but at least the method can provide
information about the temperature uniformity. User should take into account the effect of
the deposited thin-film LC on the hotplate thermal behavior.

5.2.2 Target Gases Identification

Very few commercial gas sensors are used to detect gas concentration in a mixture. These
gas sensors have applications in chemical processing, automobile combustion control and
environmental monitor. In automobile engine, the concentration of hydrocarbons in the
combustion mixture is a valuable indicator of the combustion efficiency. A small set of gas
mixture should be identified for the research. For example, mixture of toluene, acetone
and trichloroethylene is used [5.5].

5.2.3 Selectivity Improvement Based on Sensor Array

Generally speaking the thin-film metal oxide is not very selective. Researchers have been
looking into the use of sensor array to improve the selectivity over years. Array of
different sensing film or array of same sensing film but different doping can be used. The
key factor is to match the right kind of sensing thin-film to a particular gas mixture.
Therefore, sufficient gas sensitivity data of various materials or dopings must be collected
before one can design the array. Table 5.1 summarizes the sensing characteristic of
various gas sensors extracted from literatures. An automatic gas sensor measurement
system and stock of materials are also essential for this kind of research.

5.2.4 Selectivity Improvement Based on Temperature Programmed Desorption

The magnitude of a sensor response at steady state is commonly used to determine the
species concentration, while the information in the transient response is generally not
utilized [5.13]. However, the transient signal contains valuable information about the
kinetics of the chemical interaction between the gas and the sensing film. The transient
response is created by varying the temperature of the sensing film. For example, a
sinusoidal voltage is applied to a heater equipped with a SnO2 gas sensor, and the
resulting output resistance is analyzed by FFT [5.14]. The intensities of higher harmonics
indicate the characteristic changes in the presence of different kinds of gas.
<table>
<thead>
<tr>
<th>Sample</th>
<th>Gas Species</th>
<th>Conc. (ppm)</th>
<th>Sensitivity (Δ G/G)</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO₂ thin films (300nm) [5.6]</td>
<td>H₂S</td>
<td>10</td>
<td>35</td>
<td>at 500 C</td>
</tr>
<tr>
<td></td>
<td>H₂</td>
<td>100</td>
<td>7</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CO</td>
<td>100</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>SnO₂ (Pt) thin films, 300nm SnO₂, 35Å Pt [5.6]</td>
<td>H₂S</td>
<td>10</td>
<td>170</td>
<td>at 500 C</td>
</tr>
<tr>
<td></td>
<td>H₂</td>
<td>100</td>
<td>25</td>
<td></td>
</tr>
<tr>
<td>SnO₂ thin films (200nm) [5.7]</td>
<td>CH₄</td>
<td>500</td>
<td>just above threshold of sensitivity</td>
<td>at 450 C</td>
</tr>
<tr>
<td></td>
<td>C₃H₈</td>
<td>200</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>C₆H₁₄</td>
<td>100</td>
<td></td>
<td></td>
</tr>
<tr>
<td>SnO₂ (Cd) thin films, 20 to 30nm SnO₂, 1.5-15nm Cd [5.8]</td>
<td>NO₂</td>
<td>100</td>
<td>400</td>
<td>at 300 C</td>
</tr>
<tr>
<td></td>
<td>NOₓ</td>
<td>100</td>
<td>950</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CO</td>
<td>1000</td>
<td>5</td>
<td>at 400 C</td>
</tr>
<tr>
<td></td>
<td>H₂</td>
<td>1000</td>
<td>20</td>
<td></td>
</tr>
<tr>
<td></td>
<td>C₄H₁₀</td>
<td>1000</td>
<td>8</td>
<td></td>
</tr>
<tr>
<td>SnO₂ (Al₂O₃) thick films, 10 wt. % of Al₂O₃ powder [5.9]</td>
<td>H₂S</td>
<td>5</td>
<td>200</td>
<td>at 150 C</td>
</tr>
<tr>
<td>SnO₂ (Pd) thick films, 0.05 mol% of Pd [5.10]</td>
<td>NO</td>
<td>100</td>
<td>0.05</td>
<td>at 300 C</td>
</tr>
<tr>
<td>SnO₂ thin films [5.11]</td>
<td>C₂H₅OH</td>
<td>80</td>
<td>70</td>
<td>at 200 C</td>
</tr>
<tr>
<td></td>
<td>CO</td>
<td>300</td>
<td>6</td>
<td>at 300 C</td>
</tr>
<tr>
<td>SnO₂ (Pd) thin films [5.11]</td>
<td>C₂H₅OH</td>
<td>80</td>
<td>30</td>
<td>at 150 C</td>
</tr>
<tr>
<td></td>
<td>CO</td>
<td>300</td>
<td>60</td>
<td>at 100 C</td>
</tr>
<tr>
<td>Bi₂O₃ doped SnO₂ thin films, 17 wt. % of Bi₂O₃ [5.12]</td>
<td>NOₓ</td>
<td>90</td>
<td>5</td>
<td>at 200 C</td>
</tr>
<tr>
<td>SnO₂ thin films, 300nm SnO₂ [5.12]</td>
<td>NOₓ</td>
<td>100</td>
<td>1/13</td>
<td>at 200 C</td>
</tr>
<tr>
<td></td>
<td>CO</td>
<td>100</td>
<td>1.4</td>
<td>at 410 C</td>
</tr>
<tr>
<td></td>
<td>CH₄</td>
<td>100</td>
<td>1.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>H₂</td>
<td>100</td>
<td>3.2</td>
<td></td>
</tr>
</tbody>
</table>
Fig. 5.1 The temperature programmed desorption spectrum of H₂ on the (100) surface of tungsten. The three peaks indicate the presence of three sites with different desorption activation energies (from [5.17]).

Another attractive approach is to use temperature programmed desorption (TPD) techniques [5.15]. Temperature programmed desorption is an old technique to characterize the gas interaction on metal catalysts [5.16]. In a typical TPD experiments, gas is pre-adsorbed on the catalyst, and the experimental chamber is evacuated or flushed with inert gas. The catalyst temperature is then increased, allowing desorption of the chemisorbed gas into a stream of inert gas carrier. The temperature ramping is often linear. The desorbed gas is detected and plotted versus temperature. The response usually increases with time until it reaches a maximum and drops back to zero. The characteristic peak temperature is a function of the desorption action energy and therefore varies with different gases. Figure 5.1 shows an example of such TPD spectrum.

The TPD spectrum suggests that the thin-film sensor may be applied to spectroscopic analysis if we program the temperature properly. Let us suppose there are two gases A and B in a gas sensor system. Both gases have a sharp peak in the TPD spectrum as shown in Figure 5.2. The peaks are assumed to be far part. Firstly the sensor is stabilized at a suitable temperature (T₀) such that the adsorption is much faster than
Fig. 5.2 An example of gas sensing system to illustrate the idea of using TPD technique for gas detection. The top graph shows the TPD spectrum of gas A and B. The bottom time chart illustrate how the temperature is programmed. At time $t_0$ and $t_1$, the rate of change of sensor response $R_A$ and $R_B$ are measured.

desorption for both gases. This means the equilibrium coverage of the gases on the thin film surface is high. Then if the temperature is quickly programmed to the desorption peak of gas A ($T_A$), a high rate of change of the sensor response $R_A$ can be obtained. Since the desorption rate of gas B at $T_A$ is very small, the response change is mainly contributed by gas A.

Next the sensor can recover to base line by programming the temperature to $T_O$. Similarly, the temperature is quickly programmed to $T_B$ and we obtain $R_B$. For the same reason, $R_B$ is mainly contributed by gas B. We should be able to derive the concentration of the gases from $R_A$ and $R_B$. The time slot to measure $R_A$ and $R_B$ should be as short as
The cross-section of the suggested ultra-thin film integrated gas sensor. Possible so that the equilibrium condition is always kept. By doing so, this method is much faster than any other technique based on steady state response. The reliability and life-time of the sensor may also be improved.

This idea should be further investigated through experiment and deeper understanding of the underlying chemistry. The gas sensor characterization system described in Appendix B can be used to obtain the TPD spectrums of various gases on a sensor. The fast temperature programming can be implemented with the fast thermal response of the micro-hotplate; this is not the case for discrete devices. The response data can be further processed by signal processing techniques. It is expected that this method can significantly improve the selectivity of the thin-film gas sensor.

5.2.5 Modified Structure for Ultra-thin Film Integrated Gas Sensor

Physical evidence suggests that an ultra-thin sensing film is a good candidate for gas detection [5.18] The response time is expected to decrease with thinner film because bulk diffusion is eliminated. As the sensor response is mainly contributed by surface events, thinner film can obviously improve the sensitivity. However, the micro-hotplate described in this thesis cannot provide a platform for ultra-thin film deposition. We therefore propose a new structure for this purpose. Figure 5.3 shows the cross-section of the new structure. Instead of putting the sensor on the top, it is deposited right after the first CVD
oxide. Since the P+ resistors do not cause any surface profile, the film is deposited on a perfectly flat substrate. Metal is then deposited to form the electrode of the sensor. Lastly the second dielectric layer is deposited and patterned so that the sensor is exposed to air. The only challenge associated with this structure is the way to protect the thin-film sensor during the etching of metal and CVD oxide.

5.3 Reference


Appendix A  IGS003 Process Flow

For each step, an estimated number of days required is included. It takes about one month to complete one fabrication run in the Microelectronic Fabrication Center at HKUST.

1. **Wafer Preparation**
   
   1.1 Starting material: (100) n-type (PHOS), 4-7 Ω-cm, 4" wafer, 500-550 μm thick.
   
   1.2 Number the wafers with a diamond scriber.

2. **P+ Resistor Definition (3 days)**

   The **P+ resistor** are formed using boron diffusion masked by thermal oxide. In order to meet the etch stop requirement ($7 \times 10^{19}$ cm$^{-3}$), the diffusion has to be done at high temperature and for a long duration. The masking pad oxide is approximately 0.5μm thick.

   2.1 MFC cleaning procedure:

      - Dissolve organic and metallic contaminants ($\text{H}_2\text{SO}_4 : \text{H}_2\text{O}_2 = 10:1$, 120°C, 10 min).
      - Remove oxide grown during the last step ($\text{HF}:\text{H}_2\text{O} = 1:50$, 26°C, 10 min).

   2.2 Oxidation: thermal oxidation at 1050°C in wet O$_2$ for 90 min.

   2.3 Lithography:

      - Vapor priming: HMDS 10 min.
      - Resist coating: spin HPR 204, pre-bake at 105°C for 30 min.
      - Exposure: UV contact aligner in hard contact mode, light integral 40, IGS003:PDFF mask, carefully align the wafer {100} plane to horizontal pattern in mask.
      - Develop: 40 seconds in PLSI:$\text{H}_2\text{O}=1:1$, post-bake at 120°C for 30 min.
2.4 Oxide etch: 400 seconds in BOE solution.
2.5 Resist strip: 15 min in H\textsubscript{2}SO\textsubscript{4} : H\textsubscript{2}O\textsubscript{2}.
2.6 MFC cleaning procedure.
2.7 Boron diffusion: Boron disk at 1000°C for 180 min.
2.8 Deglaze and oxide strip: 600 seconds in BOE solution.

3. **Pre-Metal Oxide Deposition (about 1 week)**
3.1 7000Å undoped LPCVD oxide deposited at Vitelic (HK) Ltd, Tai Po.
3.2 Densification: 900°C for 20 min in dry O\textsubscript{2}.

4. **Contact Definition (1 day)**
4.1 Lithography:
   - Vapor priming: HMDS 10 min.
   - Resist coating: spin HPR 204, pre-bake at 105°C for 30 min.
   - Exposure: UV contact aligner in hard contact mode, light integral 40, IGS003:CONTACT mask, aligned to IGS003:PDIFF.
   - Develop: 40 seconds in PLSI:H\textsubscript{2}O=1:1, post-bake at 120°C for 30 min.
4.2 Photoresist descumming: 0.5 min in oxygen plasma.
4.3 Oxide etch: about 250 seconds in BOE.
4.4 Resist strip: 40 min in oxygen plasma.

5. **Aluminum Sputtering (1 day)**
   A multilayer of Au/(Ti/W)/Al is deposited to prevent the etching of any exposed aluminum during the EDP etch. Ti/W serves as the adhesion layer for Au.
5.1 MFC cleaning procedure.
5.2 7000Å Aluminum with 1% Si sputtering in CVC system.
5.3 Followed by 250Å of Ti/W.
5.4 Followed by 500Å of Au.

6. **Metal Definition (1 day)**
6.1 Lithography:
   - Vapor priming: HMDS 10 min.
• Resist coating: spin HPR 204, pre-bake at 105°C for 30 min.
• Exposure: UV contact aligner in hard contact mode, light integral 40, IGS003:METAL mask, aligned to IGS003:CONTACT.
• Develop: 40 seconds in PLSI:H₂O=1:1, post-bake at 120°C for 30 min.

6.2 Gold electro-etch: 40 sec in Metex L-SB, 0.1A current.
6.3 Ti/W etch: 2 min in hydrogen peroxide.
6.4 Aluminum etch: dry etch in Vitelic.

7. Passivation Oxide Deposition (about 1 week)
7.1 7000Å %3 Phosphorus LPCVD oxide deposited at Vitelic (HK) Ltd, Tai Po.

8. Pad Definition (1 day)
During the EPW etching, the bare backside silicon will also be etched. It results in thinning of the wafer and will make it mechanically fragile\(^1\). Therefore, the backside oxide deposited in the last step is retained during the oxide etch by covering it with photoresist.

8.1 Backside resist: spin HPR 204 at the back, post-bake at 120°C for 30 min.
8.2 Lithography:
• Vapor priming: HMDS 10 min.
• Resist coating: spin HPR 204, pre-bake at 105°C for 30 min.
• Exposure: UV contact aligner in hard contact mode, light integral 40, IGS003:PAD mask, aligned to IGS003:METAL.
• Develop: 40 seconds in PLSI:H₂O=1:1, post-bake at 120°C for 30 min.

8.3 Photoresist descumming: 0.5 min in oxygen plasma.
8.4 Oxide etch: 240 seconds in BOE.
8.5 Resist strip: 40 min in oxygen plasma.

Starting from here, the fabrication process splits. Refer to Table A.1 for exact flow of various split. Here we show the remaining sequence of process split Group D.

\(^{1}\) This optional step is not required if the EDP etching is done on packaged chip.
9. **Tin Dioxide Formation (1-2 days)**

9.1 Lithography:
- Vapor priming: HMDS 10 min.
- Resist coating: spin HPR 204, pre-bake at 105°C for 30 min.
- Exposure: UV contact aligner in hard contact mode, light integral 40, IGS003:SENSOR mask, aligned to IGS003:PAD.
- Develop: 40 seconds in PLSI:H₂O=1:1, post-bake at 120°C for 30 min.

9.2 Photoresist descumming: 0.5 min in oxygen plasma.

9.3 Tin dioxide deposition: 900Å SnO₂ (40% oxygen) by reactive sputtering in MCPC Denton Sputtering System (Model SJ/24LL)
- Substrate temperature: 120°C.
- Ambient: Ar:O₂ = 5:1.
- Pressure: 40m Torr.
- RF gun #2 300W.
- Time: 400 seconds.

9.4 Lift-off: immersed in Acetone for about 30 min, agitated by ultrasonic bath.

10. **Packaging (1 days)**

10.1 Die separation using wafer saw machine.

10.2 Die attach: on TO-5 or ceramic DIP.

11. **Maskless Silicon Etching (1 day)**

This step puts the bonded chips into EDP solution. The gold bond wire and ceramic case will not be etched.


11.2 EDP etch (refer to Appendix C):
- Composition: Ethylenediamine: 500ml, Pyrocatechol: 160g, Water: 160 ml, Pyrazine: 3.6 g.
- Temperature: 105°C.
- Time: 1-2 hours.
12. Wire Bonding (1-2 days)

Table A.1: Process Split for the IGS003 fabrication

<table>
<thead>
<tr>
<th>Device Group</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
<th>E</th>
<th>F</th>
</tr>
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<tbody>
<tr>
<td>Baseline up to pad definition</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Sensor Mask lithography</td>
<td>#</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>SnO₂ deposition before packaging</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
<tr>
<td>Lift-off in acetone</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
<td>X</td>
</tr>
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<td>EDP etch before packaging</td>
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<tr>
<td>Manual die separation</td>
<td>X</td>
<td>X</td>
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<tr>
<td>Automatic die separation at Motorola</td>
<td>X</td>
<td>X</td>
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<td></td>
<td></td>
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<tr>
<td>Wire bonding</td>
<td>X</td>
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<td></td>
</tr>
<tr>
<td>EDP etch after packaging</td>
<td>X</td>
<td>X</td>
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<tr>
<td>SnO₂ deposition after packaging</td>
<td>X</td>
<td>X</td>
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</tbody>
</table>

† In Groups A and C we deposit SnO₂ on packaged chip without any lithography. Wafer saw machine has high pressure water cleaning which will damage the microstructure. Therefore, in Groups A and B we try to separate the die manually. Group D is the normal run while Groups E and F are reserved for later used.

‡ During the exposure, the left half of the wafer is covered so that resist remains there after the development. The SnO₂ deposited on the left half will be removed by the following lift-off process.
Appendix B  Automatic Gas Sensor Characterization System

A precision gas sensor characterization system is needed to measure accurately the gas sensor response [B.1]. The system must be able to simulate a range of ambient conditions that the gas sensor is likely to encounter. The system must be highly automated in order to measure dynamic response. The complete system is enclosed within a fuming cupboard and therefore ensure safety during the measurement.

B.1 Features

The major requirements of the system were identified and listed below:

- Simultaneous testing of multiple gas sensors, various types of packages should be supported (e.g. TO-5, DIPs).
- Precise flow control of test gas (ppm level) and ambient gas (e.g. N₂, air).
- In-situ gas concentration analysis.
- Moisture regulation.
- Small sample volume for even and fast gas mixing.
- Automated control of gas flow, gas sensor temperature and measurement of sensors response.

We designed the characterization system based on the above specifications. The schematic of the system is shown in Figure B.1.

B.2 Gas Concentration Control

The system must be able to control gas concentration up to ppm level. Mass Flow Controllers (MFC) of range 3-10 sccm control the flow of test gases and MFC of range larger than 10 sccm control the flow of air or other ambient gas. Depending on the availability, the gas sources can be gas bottles or permeable gas sources. The later has to
be carried by other gas and the flow rate can be higher. For very low concentration, the
gas can be pre-mixed with other ambient gas. The exact gas concentration is monitored by
gas mass spectrometer which is directly connected to the chamber. Moisture control is
also important because it affects most sensors. Water vapor is evaporated in another
chamber and carried by ambient gas. The humidity control is effected by the heating
temperature.

B.3 Test Chamber

The test chamber design is shown in Figure B.2. The chamber is vacuum sealed by the top
cover. The sensor chips are plugged into the socket board which includes sockets for TO-
5, DIP 14 pin and Figaro sensor package. The signals are connected to the outside
through the vacuum leadthroughs. Gas inlets and outlets are welded to the side wall of the
chamber. The chamber is pumped down to low vacuum by a mechanical pump before
each measurement. The small electric fan mixes the gas inside the chamber.

B.4 Computer Control and Data Acquisition

The gas flow is controlled by the National Instrument multi-IO board installed in a PC.
The signals from the board control the MFC flow rate, vacuum pump on-off and gas
valves on-off. The IO board output signals can also control the sensor temperature and
bias control. Another approach is to control external precision power supply through
GPIB interface. Similarly, the sensor response data can be measured using the IO board
input or from external digital multimeter through GPIB interface.

B.5 Test Software

The testing software being developed should control the the multi-IO board and the GPIB
interface. It should allow the configuration of test sequence, gas concentration, sensor
signals and test mode. The general sequence of test may be purging, evacuation by pump
down, ambient gas flow in, sensor temperature control, test gas flow in, measurement
cycle, residual gas analysis and finally purging. The software should allow users to specify
the test sequence. The gas concentration module should be able to calculate the MFC
flow rate and duration based on the gas sources type and user input gas partial pressure. Since the sensor connection may vary from time to time, the sensor signal module should allow flexible signal mapping. It should read in the temperature calibration data of each sensors and use the data in controlling the sensor temperature during measurement. Finally, the software should allow flexible test mode. Two major modes are steady-state response and dynamic response of changing gas concentration and sensor temperature. The programmed temperature desorption technique described in Chapter 5 should also be supported.

B.6 Reference

Gas Sensor Test System Schematic

Fig. B.1  Schematic of the automated gas sensor characterization system.
Fig. B.2  The test chamber design in the automatic gas sensor characterization system.
Appendix C  Experimental Procedure of EDP Silicon Etch

C.1 Composition

500 ml Ethylenediamine, 160 g Pyrocatechol, 160 ml Water, 3.0 g Pyrazine 3.0 g

C.2 Procedure

1. Clean the reflux system if necessary.

2. EDP does not etch silicon dioxide. Therefore, a 20 second 50:1 HF dip is used to remove native oxide from the silicon surface.

3. Put the N₂ purger into the breaker.

4. Prepare the etchant in the following order:
   - weigh pyrocatechol and place in the reflux breaker.
   - weigh pyrazine and add it to the reflux breaker. Cover the breaker because pyrazine is very volatile.
   - add water into a measuring cylinder.
   - add ethylenediamine into another measuring cylinder.

5. Pour both the water and ethylenediamine into the reflux breaker. Note that the mixing reaction is highly exothermic and handle ethylenediamine with care, as it is a potent carcinogen.

6. Cover the breaker immediately. Connect the N₂ purger, turn on the hotplate, circulating water and purging N₂. Be sure to open the top end of condenser to release pressure or just cover it with a filter paper. Insert the thermometer into the remaining inlet. The operating temperature is around 95°C.

7. Adjust the heater control until the bath temperature is stabilized.

8. Place wafers into teflon cassettes provided. Always wear sufficient protection (face mask, vapor filter) when doing this.
9. Put on fresh plastic gloves and lower carefully the cassette into the reflux breaker. Start timing the etch.

10. Since the system can not stabilize the temperature of the solution, one must manually control the heater knob. Never apply too much heat power to the system because it needs much longer time to cool down then heat up. Higher N₂ purging rate will improve the stirring and can result in higher etch rate.

11. The solution temperature actually varies during the etching. The experimenter should measure the temperature periodically. The average temperature is used as the reference.

12. When the etch is complete, lift the cassette and close the reflux system immediately. Place the cassette in rinse tank and initiate the rinse cycle. Shut off the heater.

13. Note that EDP is an excellent dye. A very small trace of it can turn a whole tank of water into black. Therefore, the user should clean up and dry the station thoroughly after the experiment.

14. For the disposal of the chemical, please notice the following:
   
   - The solution has to be freshly prepared every time because the system still allow some evaporation of the solution from the top end of the condenser.
   - Ask the technician to give you the waste can which is intended for organic solution. Use a manual pump to aspirate the solution into the waste can. Always wear sufficient protection (face mask, vapour filter) when you are doing so.