DESIGN OF MICROHOTPLATE BASED GAS SENSING SYSTEM

by

ZAINI ABDUL HALIM

Thesis is submitted in fulfillment of the requirements
for the degree of
Doctor of Philosophy

May 2008

ACKNOWLEDGEMENTS

First and foremost, I would like to express my utmost gratefulness to God Almighty for giving me the strength, wisdom and perseverance in successfully accomplishing my research.

I am extremely grateful to my supervisor, Assc. Prof. Dr. Othman Sidek for giving me the opportunity to do this PhD research under his grant and also for his support and supervision. I also would like to thank Dr. Tun Zainal Azni b. Zulkifli, Assc. Prof. Dr. Zaidi b. Mohd Ripin, Assc. Prof. Dr. Ishak b Haji Abd Azid from School of Mechanical Engineering and Dr Zuhailawati Bt. Hussain from School of Material Engineering. Their valuable comments and ideas have been most useful in this project. I am also indebted to Prof. Kamarulazizi b. Ibrahim for allowing me to use the instruments in the Physics Lab during the post processing period.

My thanks are also due to many individuals namely En. Ismahadi b. Syono from MIMOS Berhad for helping me to fabricate the device, En Sufian b. Saad from SIRIM AMREC for helping me in coating process, my friends, technicians, administrative staffs of Electrical and Electronic Department and many others who have been involved directly or indirectly throughout my research.

Special thanks are due to my parents, who have continuously encouraged me to complete this thesis.

To my husband Rizal B. Azodin, thank you very much for your moral support, your opinions and your ideas to complete this thesis and also for being patiently

supporting my career in life. To my sons Irfan Hakim, Iqbal Hakim, Ikhwan Hakim and Idlan Hakim, all of you are always in my mind.

Last but not least, I would like to express my sincere gratitude to National Science Fellowship for the scholarship I received in pursuing this Doctoral Philosophy Degree.

TABLE OF CONTENTS

CHAPTER 1: INTRODUCTION

CHAPTER 2: LITERATURE REVIEW

CHAPTER 3: DESIGN, FABRICATION AND CHARACTERIZATION OF MICROHOTPLATE

CHAPTER 4: SENSOR DEVELOPMENT AND CHARACTERIZATION

CHAPTER5: DESIGN AND DEVELOPMENT OF ELECTRONIC CIRCUITRY

CHAPTER 6: RESULT AND DISCUSSION

CHAPTER 7: CONCLUSION

LIST OF TABLES

LIST OF FIGURES

LIST OF PLATES

LIST OF ABBREVIATIONS

ADC	Analog Digital Converter
AMREC	Advance Material Research Centre
BiCMOS	Bipolar Complementary Metal Oxide Semiconductor
CMOS	Complementary Metal Oxide Semiconductor
EDP	Ethylene Diamine Pyrochatechol
FPGA	Field Programmable gate Array
GDS	Graphic Design System
IC	Integrated Circuit
KOH	Potassium Hydroxide
MEMS	Microelectromechanical System
PC	Personal Computer
PLD	Programmable Logic Device
RF	Radio Frequency
SPSS	Statistical Package for the Social Science
TMAH	Tetra Methyl Ammonium hydroxide
USB	Universal Serial Bus
VOC	Volatile Organic Compound
VHDL	Very High Speed Hardware Description Language

Design of Microhotplate Based Gas Sensing System

Abstract

The purpose of this research is to design, fabricate and characterize a microhotplate based gas sensing system. Wet etching with EDP as an etchant is implemented to realize the suspended structure of microhotplate. Based on the graph (metal plate resistance versus heater voltage), the gradient can be analyzed in order to see if the microhotplate has gradually became a suspended structure. With polysilicon as a heater material, the microhotplate platform requires 40miliwatt to heat up the sensing film until 350°C. Approximation technique (by using aluminium melting point) is used for thermal calibration of microhotplate. The main sensing region is covered with 120µm x 120µm SnO_2 thin film and WO_3 thin film which are deposited by RF sputtering technique. Tin and Tungsten targets have been used and oxygen is purged into the chamber during deposition process in order to get tin oxide thin film and tungsten oxide thin film. 1 sccm of oxygen, 2 sccm of oxygen and 3 sccm of oxygen have been used in the experiments. The results show that tin oxide with 1sccm of oxygen and tungsten oxide with 3 sccm of oxygen exhibits acceptable response, time recovery and as well as high sensitivity. The sensitivity to gas depended strongly on the uniformity of grain size, and the optimum mean grain size of SnO_2 is about 50nm, observed by SEM. The sensors have been tested using acetone, ethanol and methanol and the response time of the sensor is 45s including the vaporize time.

Rekabentuk Sistem Pengesanan Gas Berasaskan Plat Pemanas Mikro

Abstrak

Tujuan kajian ini adalah untuk merekabentuk, fabrikat dan mencirikan system pengesan gas berasaskan microhotplate. Teknik mikromesin pukal, menggunakan EDP telah digunakan untuk mendapatkan struktur microhotplate yang tergantung. Berdasarkan kepada graf rintangan pada metal plat melawan voltan pemanas, kecerunan yang didapati boleh digunakan untuk analisis samada platform tersebut telah menjadi terampai sepenuhnya ataupun belum. Dengan menggunakan polisilikon sebagai pemanas, platform mikrohotplate memerlukan 40 miliwat untuk memanaskan filem pengesan sehingga 350°C. Kawasan pengesanan utama yang bersaiz 120µm x 120µm, ditutupi dengan filem nipis SnO_2 dan filem nipis WO_3 yang mana ia didepositkan melaui proses RF sputtering. Target daripada tin dan tungsten digunakan dan oksigen dilalukan supaya ia dapat bertidakbalas dengan tin dan tungsten untuk membentuk tin oksida dan tungsten oksida. 1 sccm oksigen, 2 sccm oksigen dan 3 sccm oksigen digunakan dalam eksperimen. Keputusan menunjukkan tin memerlukan 1 sccm oksigen manakala tungsten pula memerlukan 3 sccm oksigen untuk memberi keputusan yang baik. Kepekaan pengesan tersebut bergantung kepada saiz butiran tin oksida dan tungsten oksida yang seragam. Saiz butiran yang optimum bagi Sn adalah lebih kurang 50nm, dilihat menggunakan SEM. Pengesan tersebut diuji dengan menggunakan acetone, ethanol dan methanol dan masa tindak balas yang diper;ukan ialah 45 saat termasuk masa pemeruwapan bagi acetone, ethanol dan methanol.

CHAPTER 1

INTRODUCTION

1.1 Microelectromechanical System

By definition MEMS components contain micrometer-dimensioned elements, usually with a moving part, sometimes a solid mechanical, sometimes a fluid one and usually integrated together with at least some electronic circuitry. The electronic circuitry may be only a piezoresistor network or a capacitive element to transducer mechanical motion into an electrical signal but it can be much more than that. MEMS are usually produced using integrated circuit technology that uses lithography and etching. Besides silicon, glass, quartz and plastic substrate are sometimes applicable as a MEMS's substrate.

Pressure sensors with bulk etched silicon structure were the first wave of MEMS commercialization started in the late 1970s and early 1980s. Pressure sensors consist of a thin silicon membrane. The silicon membrane will deform under pressure and it will affect a piezoresistive track laid on its surface and the change is used to transform the pressure into an electronic signal. Subsequent devices include the capacitive sensed moving-mass accelerometer used to trigger airbag deployment in automobiles and gyroscopes for orientation (Clarke, 2002).

A second wave of commercialization arrived in the 1990s, mainly focused on PC and information technology. Video projection is one of the products in this era. It was introduced by Texas Instrument that is based on electrostatic actuated tilting micro mirror arrays. The thermally operated inkjet print head is another product that remains a high volume application until now.

The third generation of MEMS commercialization is a micro-optics as an accompaniment to fiber optic communication- by way of all optical switches and related devices. Other MEMS application that could be the inspiration and beneficiary of the fourth wave of the commercialization include electronic nose, biological and neural probes, called lab-on-a chip biochemical and drug development systems and microscale drug-delivery systems. Table 1.1 shows the demands for MEMS applications.

Table 1.1: The demands for MEMS applications (Clarke, 2002)

Application	**Demands**
Disposable blood pressure sensing	Approximately 20 million units per year
Automotive ECU pressure sensing	Approximately 40 million units per year
Accelerometers (mainly airbag)	Approximately 70 million units per year
Inkjet print head	600 to 700 million unit per year
Hard disk drive read-write heads	Approximately 1 billion units per year

1.2 Electronic Nose

The development of an electronic nose using MEMS technology has started since 1990s. Electronic nose consists of a mechanism for chemical detection, such as an array of electronic sensors and a mechanism for pattern recognition such as neural network. Electronic noses have been around for several years but have typically been large and expensive. Current research is focused on making the devices smaller, less expensive and more sensitive. These targets can be achieved using MEMS technology.

Electronic noses were originally used for quality control applications in the food and cosmetics industries. Aroma and taste of foods are due to the interaction of human sensory organs with the volatile and semi-volatile organic chemical constitutes in food materials. Some food may contain dozens or hundreds of these volatiles flavor contributing chemicals which can be analyzed using GC/MS (gas chromatography/mass spectrometry analysis). Unlike chromatography techniques, the electronic nose does not attempt to separate or resolve all individual volatile components. It uses an array of sensors that responds to each volatile chemical much like the human nose functions (Marsili, 1995).

The electronic nose is also needed in shuttle and space station. Ammonia is just one of about forty or fifty compounds necessary on the shuttle and space station, which cannot be allowed to accumulate in a closed environment. It flows through pipes, carrying heat generated inside the station into space. Ammonia helps to keep the station habitable but it is also poisonous. If it leaks, the astronauts will need to know quickly. Ammonia becomes dangerous at a very low concentration, (just a few parts per million). However humans cannot sense it until it reaches about 50 ppm (Miller, 2004).

Another application of the electronic nose is in healthcare. Approximately three million people worldwide die of TB each year. Traditional microbiological diagnostics identify bacteria through a process of culture in growth media followed by biochemical tests. The process is often lengthy and costly. An electronic nose can smell tuberculosis bacteria. The approach is based on identifying certain compounds in the gases emitted by the tuberculosis bacteria in clinical samples. The electronic nose invented at Cranfield University in Bedfordshire can produce a reliable result in only four hours whereas laboratory methods of confirming infection take two days, which can make the difference between life and death in some cases (BBC News, 2001).

All of the applications mentioned above will not be successful without good sensors and good performance of data acquisition system. Several researchers have previously reported on the use of gas sensors in arrays, such as metal oxides (Srivastava, 2003; Lee et al., 2001; Szczurek et al., 1999), electrochemical sensors (Mosier-Boss and Lieberman, 1999), conducting polymers (Guadarrama et al., 2002), quartz crystal microbalance (Chang and Shih, 2000) and hybrid sensors arrays (Cui et al., 2000). In this project, a gas sensor system is developed and has been tested with volatile organic compounds such as acetone, ethanol and methanol. These compounds produce series health effects such as liver or nervous system problems, reproductive difficulties and increase risk of cancer (Zhu et al., 2006)

1.3 Metal Oxide Sensor

Metal oxide sensors have good sensitivity to organic vapors for a very broad range of chemical compounds (Barenttino et. al., 2006),(Kovacs, 1998). Since many sensors can response to a single volatile compound but in different magnitude, sensor arrays must be employed. For proper functioning, metal oxide sensors are usually heated to between 175° and 425°C. The electrical resistance of the sensor changes in the presence of an odor, with the magnitude of the response dependent on the nature of the detected molecule and the type of metal oxide used in preparing the sensor. Response time of metal oxide sensors is between 10 and 120 seconds.

Several metal oxides like tin oxides, indium tin oxides, zinc oxides and titanium oxide (Benkstein et. al., 2006) are known as transparent conductive oxide. Such oxides are very sensitive to volatile organic gas and change their resistance upon exposure to analyte gases (Graf et al., 2004). Among these materials, tin oxide has unique properties in chemical inertness, stability to heat treatment and mechanical hardness (Matsui et al., 2003). Tin oxide is also cheap, reliable and convenient for domestic carbon monoxide gas monitoring. However the primary drawbacks associated with tin oxide gas sensor are cross sensitivity and large power consumption. Cross sensitivity sometimes will cause false alarm and large power consumption make it impossible for a portable gas monitors (Han et al., 2002).

To overcome these problems many researchers are focusing on the microhotplate as a platform of tin oxide gas sensor. These are reported by Semancik et. al., (2001); (Affridi et. al, 2004), (Chan et. al.,2002). Accordingly, much effort has been made to coat tin oxide as an active layer of the sensor. Several researches have previously reported on the technique development of tin oxide gas sensor such as screen printing (Riviere et al., 2003), thermal oxidation (Shim et al., 2002), pulse laser deposition method (Kim et al., 2001) and chemical vapor deposition (Semancik et. al., 2001).

1.4 Data Acquisition System

Data acquisition is a process used to collect information to document or analyze some phenomena. A simple example of data acquisition system is logging the temperature of an oven on a piece of paper. As technology progressed, this type of process has been simplified and made more accurate, versatile and reliable through electronic equipment.

Resolution refers to the smallest signal increment that can be detected by a data acquisition system. Resolution is determined by the analog to digital converter. Hence Analog digital converter is the heart of most data acquisition systems. For example 12 bit analog digital converter will produce a system with 12 bit resolution, one part in 4096 resolution or 0.0244% of full scale.

Sample rate is the speed of data acquisition system which is typically given by the speed of the analog to digital converter. There are four types of data acquisition system:

1) Serial communication data acquisition system
2) Universal Serial Bus (USB) data acquisition system

3) Data Acquisition plug in board
4) Parallel port data acquisition system

RS232 is the most common standard for serial communication system. However it only supports communication to one device at a time and the transmission distance is only 50 feet. Another standard for serial communication is RS485. It is more flexible in that it can support to more than one device at a time. Transmission distance can be up to 5000 feet.

The USB is a new standard for connecting data acquisition systems to a PC. There are some advantages of USB over serial port and parallel port, including higher bandwidth and the ability to provide power to the peripheral device. Since USB connections can supply power, only one cable is required to link the data acquisition device to the PC.

Computer plug-in board is another type of data acquisition system. The advantage of this system is high speed since it is connected directly to the computer bus. Each board installed in the computer is addressed at a unique input/output map location. The I/O map in the computer provides the address locations that are used by processor to access the specific device as required by its program.

Parallel port can also be used to connect data acquisition system to PC. The system can support very high sample rate. However the distance between the computer and the data acquisition device is limited to a few feet.

1.5 Motivation

As mentioned, there are many applications of the electronic nose in life. The performance of the electronic nose depends strongly on gas sensor's performance. Sensor's technology is always changing in order to get better performance. Metal oxide sensor is one of the broadest and oldest type of gas sensor. The adsorption of gases onto certain metal oxide can greatly modulate their resistivities. MEMS is a current technology to miniaturize the sensor device into micron size and to replace the traditional bulky electrodes in gas sensor application.

Microhotplate is a platform using MEMS technology and applicable to metal oxide gas sensors. There are many techniques of deposition of metal oxide such as RF sputtering with metal target (Stankova et al, 2006), DC magnetron sputtering using metal target (Jin et al, 2006) and chemical vapor deposition process (Affridi et al, 2002). This project will propose RF sputtering technique using metal target to deposit metal oxide on microhotplate platform. Metal target is cheaper than metal oxide target and metal oxide target is easier to cleave compared to metal target.

Gas sensor without data acquisition system is of little use. Data must be collected automatically for further analysis such as for pattern recognition system.

This approach can be performed using digital circuit. FPGA is a current technology in digital circuit. FPGA are reprogrammable devices, where making the change from one digital circuit to another is made by simply downloading a new interconnection file, greatly facilitating the design and debugging of complex digital circuit.

By combining these technologies (metal oxide sensor, microhotplate platform and FPGA technology), a portable, low power consumption, battery powered and cheaper electronic nose can be produced.

1.6 Research Objectives

The MEMS technology in realizing a smaller device to give a faster response constitutes the backbone of the research conducted in this thesis and motivates the development of microhotplate based gas sensing system. Apart from microhotplate structure, the metal oxides as the active elements of the sensor are researched for application of gas sensing system. In summary, this research work is geared towards achieving the following objectives:

1. To design a microhotplate based gas sensing system.
2. To fabricate a microhotplate on silicon wafer
3. To characterize the microhotplate.
4. To develop a metal oxide layer using metal target in RF sputtering technique.
5. To develop data acquisition system that is applicable to microhotplate based gas sensing system.

1.7 Research Scope and Methodologies

The goal of this research is to study the development of microhotplate based gas sensing system which is a sub-component of electronic nose. The microhotplate based gas sensing system should have the following features such as portable, low power consumption, battery powered and cheap. The motivations are to develop metal oxide layer using RF sputtering with metal target on microhotplate platform and develop some measurement techniques during microhotplate calibration process. To evaluate the capability and applicability techniques, a series of experiments have been performed.

The microhotplate is first designed using ANSYS software. The process definition file is defined using MEMSPro software in order to get a suspended structure of microhotplate. Suspended structure is very important for thermal isolation. The GDS file is generated and sent for fabrication process.

Dicing process is performed once the fabrication process is completed. This process is followed by etching process. Wet etching with EDP as an etchant is implemented to realize the suspended structure of microhotplate. Based on the graph (metal plate resistance versus heater voltage), the gradient is analysed in order to see if the microhotplate has gradually became a suspended structure.

This project only concentrates on tin oxide and tungsten oxide. These oxides are deposited using RF sputtering technique with tin target and tungsten target. The discharge gas is oxygen and argon. Oxygen concentration is varied in order to get tin oxide sensor and tungsten oxide sensor that has good performance.

Metal oxide sensor works well at 350°C. Approximation technique is used for thermal calibration of microhotplate. It is known that metal (aluminium) plate melts around 500°C. Hence continuity test across the metal plate is performed while increasing the heater voltage to increase the temperature of microhotplate. When the reading of continuity test is open load, it indicates that the metal plate has already melted. The voltage that required to heating up the sensor until 350°C can be calculated by using this approximation technique. The proposed process and techniques are then tested using acetone, ethanol and methanol.

1.8 Thesis Organization

Chapter 2 covers a literature review of this research. The main topics discussed here are electronic nose, research that has been conducted, silicon crystal structure, MEMS technology, metal oxide sensor, microhotplate, coating process and data acquisition system.

Chapter 3 describes the research methodology used in this project. It occupies the designing process using ANSYS and MEMSPro software, post processing process, vapor concentration and the overall experimental set up for measurement procedure.

Chapter 4 describes on the design and development of the data acquisition system hardware circuitry in detail and the read out circuit for sensor implementation. Data acquisition system which is developed by using Xilinx IC and VHDL code, is used to program the circuit.

Chapter 5 presents the coating process using RF sputtering and tin as a target in order to deposit tin oxide as an active layer of the sensor. The thickness of the tin oxide is estimated using spectroscopic reflectance and SEM is used to confirm the result. The characterization of the overall sensor is presented in this chapter.

Chapter 6 presents the results and discussion of the preceding chapters (Chapter 3, chapter 4 and chapter5). Further discussed in this chapter is on the test carried out by the sensors using ethanol, methanol and acetone. The performance of the sensor is also analyzed and discussed.

Lastly chapter 7 outlines the conclusion of the research work, problems encountered and suggestions on some of the future possibilities to improve and up grade the sensor and the referred system.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

An odor is composed of molecules, each of which has a specific size and shape. Each of these molecules has a correspondingly size and shape receptor in the human nose. When a specific receptor receives a molecule, it sends a signal to the brain and the brain will identify the smell associated with the particular molecule. Gas sensing system works in a similar manner by substituting sensors for the receptors and transmitting the signal to a program for processing. Basically gas sensing system consists of sensors array and data acquisition system. This chapter will discuss about the gas sensing system (focusing on researches that have been conducted), metal oxide gas sensor, thin film coating, microhotplate platform and data acquisition system based on FPGA.

2.2 Gas Sensor

Sensors are electronic devices that gather information from the environment and acts as a transducer, converting recognized energy or physical signal received into a form in which it can be easily processed. The physical signal involved in sensing processes include chemical, electrical, magnetic, mechanical, radiant and thermal. Table 2.1 shows a list of some common transducers and physical signal which can be measured (Kovacs, 1998).

Table 2.1: Physical Signal and Transducers

Physical Signal	**Transducer**
Temperature	Thermocouples Resistive Temperature Devices (RTDs) Thermistors
Light	Vacuum Tube Photo Sensor
Sound	Microphone
Force and Pressure	Strain Gauges Piezoelectric Transducer
Position and Displacement	Potentiometer
Fluid	Rotational Flowmeters
PH	pH Electrodes
Resistance	Metal oxide sensor

A sensor comprises a material with flexible physical properties that changes according to the concentration of some chemical species. Consequently, this in turn will transform the physical signal into an electrical or optical signal which is recorded by a device. These analog data will be collected and digitized into digital signal by data acquisition system.

The most important characteristic of the sensor is the ability to adsorb and desorb the tested molecules. Adsorption is a process where the sensor would collect and hold the molecules of the analytes on its surface and produce the measurable change in the sensor. Desorption is a process where the molecule is removed from the surface of the sensor during cleaning process.

In order to support an effective gas sensing system, the sensor element must fulfill several requirements. It needs to be selective to analytes in any of atmospheric including high humidity environment. Besides, the signal to noise ratio should be higher and the signal should have a large dynamic range. It must be able to detect at high speed to ensure rapid response to potentially hazardous leaks. Another criterion is it must consume low power since low power consumption is very important for portable instrumentation (Dimoe, 2000).

There are many types of gas sensors such as quartz resonator microbalance (Monte et al., 1999), (Nanto et al, 1999), quartz crystal microbalance and metal oxide sensor. In this project, microhotplate platform for metal oxide sensor has been developed using MEMS technology and the fabrication process is compatible to CMOS process.

2.3 Researches that have been conducted

Current research is focused on making the device smaller, less expensive and more sensitive. Current technologies involved to achieve the targets are MEMS technology. Sensors can be built using MEMS technology and data acquisition system can be designed and implemented on FPGA.

Afridi (Afridi et al., 2002) and Semancik (Semanchik et al., 2001) have designed microhotplate structure using CMOS technology. Tin oxide and titanium oxide have been deposited on the microhotplate using LPCVD method. Both of them used bulk micro machining technique to build a suspended structure.

Microhotplate has also been designed by Chan (Chan et al.,2002). Surface silicon micro machining technique is used to build a suspended structure. The tin oxide is sputtered and patterned using lift-off photolithography technique. He has reported that the sintering process will help to stabilize the film. He also discovered that the sintering temperature varied from 400°C to 700°C. De Voe (DeVoe et al., 2003) has developed the microhotplate and he has found that by reducing the grain size of tin oxide will improve the sensitivity of the sensor.

Mikawa (Mikawa et al., 2002) studied the SnO2 thick films using SnO2 powder. The heater is made of platinum, which is not compatible to CMOS process. He also found that the sensitivity and selectivity to odorless gases depended strongly on the grain size of SnO2. Wang (Wang et al., 2002) has studied about tin oxide sensor. The tin oxide has been prepared by the sol-gel method. However the preparation procedure is quite complicated and the experimental conditions are difficult to control.

Lee (Lee et al., 2002) has developed a tin oxide sensor using thermal evaporation process and where the sensor was oxidized in an electric furnace at 700°C for 1 hour in oxygen atmosphere. Tao (Tao et al., 2002) has developed tungsten oxide sensor using RF sputtering method. The wafer is annealed at 650°C in order to get better performance. Matsui (Matsui et al., 2003) has studied about tin oxide film growth in chemical vapor deposition. Tin oxide films were deposited through hydrolysis reaction from stannic chloride and water.

Abdul Rahman (Abdul Rahman, et al., 2004) has developed a data acquisition system and ANN (artificial neural network) to perform pattern recognition task. The whole system has been developed using Philips 89C52 microcontroller as the embedded processor.

In this project, RF sputtering method is used to deposit tin oxide and tungsten oxide on microhotplate structure. Tin target and tungsten target will be used, since tin target and tungsten target have higher deposition rate than tin oxide target and tungsten oxidet target. The reason for this is tin and tungsten are conductors whereas tin oxide and tungsten oxide are insulators. Tin and tungsten are hard material compared to tin oxide and tungsten oxide that are easy to cleave and break down. Furthermore tin and tungsten are cheaper than tin oxide.and tungsten oxide. For data acquisition part, FPGA will replace 89C52. Since some of components can be programmed into FPGA, the size of board area for the whole circuit will be reduced.

2.4 Microelectromechanical System (MEMS) Technology

MEMS are small integrated device or system that combines electrical and mechanical components. The range in size is from micrometer to millimeter and there can be any number of components, from a few to millions in a particular system. MEMS extend the fabrication techniques developed for the integrated circuit industry to add mechanical elements such as beams, gears, cavity, diaphragm and springs to device.

The idea of MEMS comes after the invention of integrated circuit. In 1947, Bell Telephone Laboratory has found the transistor technology. In 1958, Jack Kilby from Texas Instrument built the first Integrated Circuit, using germanium device. It consisted of one transistor, three resistors and one capacitor. The IC was implemented on a sliver of Germanium that was glued on a glass side. Later, in the same year, Robert Nyoce from Fairchild Semiconductor built the planar double diffuse silicon IC. The complete transition from the original germanium transistors with grown and alloyed junctions to silicon (Si) planar double diffused devices took about 10 years (Vittorio, 2001)

Silicon becoming more popular as an electronic material was due to its wide availability from silicon dioxide (sand) resulting in lower material cost relative to other semiconductor. Due to the availability of SiO_2, much effort was put into developing a micro-sensor from silicon. The first micro-sensor, which has also been the most successful, was the Silicon pressure sensor. The first high volume of pressure sensor was marketed by National Semiconductor in 1974 (Vittorio, 2001).

Around 1982, the micromachining technique is used in silicon micro-sensor for designing the fabrication of micromechanical parts like pressure sensor diaphragms or accelerometer suspension beam. The micromechanical parts were fabricated by selectively etching areas of the silicon substrate away in order to leave behind the desired geometries. MEMS fabrication technology is based on IC fabrication technology and some extra processes are added to get the three dimensions structure and the structural parts of a device. The major steps in IC fabrication technology are film growth, doping, lithography, etching, dicing and packaging (Gardner, 2001).

For MEMS fabrications, there are three more processes included, bulk micromachining, surface micromachining and wafer bonding (Kovacs, 1998). Packaging in MEMS strongly depends on the application environment.

In short, MEMS can be produced using CMOS and BiCMOS technology in combination with compatible micromachining and thin film deposition steps. The extra MEMS steps can follow the regular CMOS process which is called post CMOS or pre CMOS. It also can be performed between the CMOS steps that are called intermediate processing (Baltes et al., 2001).

In pre CMOS approach, the sensing structures are formed before regular CMOS process. In this case the micromachining technique must fulfill the stringent criteria especially regarding the contamination that could enter microelectronic processing line afterwards. In intermediate processing, the CMOS processes sequence is interrupted for additional thin film deposition or micromachining steps. This approach is usually used to implement surface micromachined polysilicon based structure in CMOS technology.

In post processing approach, two techniques are pursued. The MEMS structures are completely built on top of finished CMOS substrate leaving the CMOS layers untouched. In the second technique, the MEMS structure can be obtained by machining the CMOS layer after the completion of the regular CMOS sequences. Microhotplate is performed using post-processing etching.

2.4.1 Bulk Micromachining

Bulk micromachining is used to realize micromechanical structures within the bulk of silicon wafer by selectively removing the wafer material (Fu et al., 2002). Structures that can be realized using this process include beams, diaphragms, grooves, orifices, springs, gears, suspensions and a great diversity of other complex mechanical structures. The etch process employed in bulk micromachining comprises one or several of the following techniques:

1) wet isotropic etching
2) wet anisotropic etching
3) non-plasma isotropic dry etching
4) reactive ion etching (RIE)-dry etching

2.4.1.a Wet Isotropic etching

Isotropic etchants etch in all directions at nearly (and sometimes exactly) the same rate. Pits and cavities with rounded surface (even nearly perfectly hemispherical shapes) can be obtained with good agitation. Figure 2.1 shows the isotropic etch cross sections using SiO_2 as a mask. The most common wet isotropic silicon etchant are nitric acid

(HNO_3) and acetic acid (CH_3COOH). A drawback of this etchant is that it attacks SiO_2 (as a mask) relatively quickly (30 to 70nm/min).

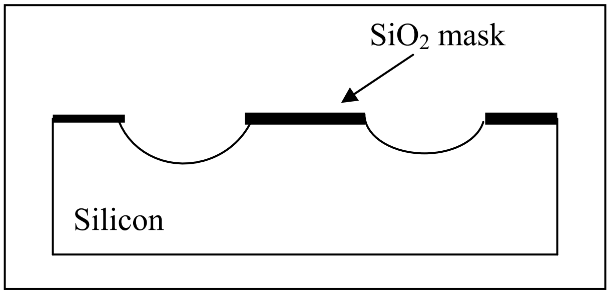

Figure 2.1: Isotropic etch cross section

2.4.1.b Wet anisotropic etching

Anisotropic etchant etch much faster in one direction than in another. Figure 2.2 illustrates the anisotropic etch cross section.

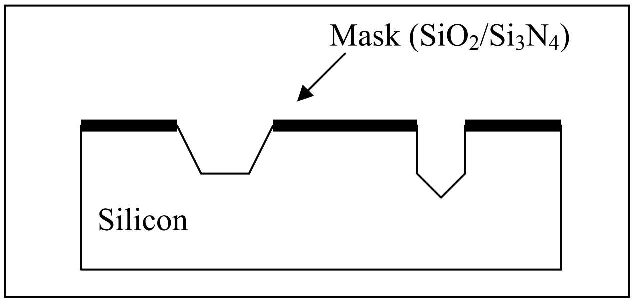

Figure 2.2: Anisotropic etch cross section

The common wet anisotropic etchants are KOH (potassium hydroxides), TMAH (tetra-methyl ammonium hydroxide) and EDP (ethylene diamine pyrochatechol) (Suehle,1993).

Table 2.2 Example of KOH etchant formulation for 100 silicon etch rate

Formulation	**Temperature °C**	**Etch Rate (µm/min)**	**(100)/(111) Etch Ratio**	**Masking Films (etch rate)**
KOH (44g) Water,Isopropanol (100ml)	85	1.4	400:1	SiO_2(1.4nm/min) Si_3N_4 (negligible)
KOH (50g) Water, Isopropanol (100ml)	50	1.0	400:1	SiO_2(1.4nm/min) Si_3N_4(negligible)
KOH(10g) Water(100ml)	65	0.25 to 1.0	-	SiO_2 (0.7 nm/min) Si_3N_4 (negligible)

Table 2.2 shows the example of KOH etchant formulation for 100 silicon etch rate (Madou, 2002). Isopropyl alcohol can be added as a diluent to increase selectivity. SiO_2 or Si_3N_4 can be used as a masking film. For KOH, the silicon etch rate is 1.4um/min and the SiO_2 etch rate is 1.4nm/min, which is quite negligible. A KOH at 80°C produces a uniform and bright surface. Bubbles are seen emerging from the silicon wafer while etching in KOH.

Meanwhile, with EDP, a variety of masking materials can be used like SiO_2 Si_3N_4, Au, Cr, Cu, and Ag. The etch rate of SiO_2 is much slower than KOH. The ratio of etch rates between silicon and SiO_2 can be 5000:1, corresponding to about 2Å/min of SiO_2 compared to 1um/min of silicon. The etch rate slows down at a lower boron concentration than with KOH. If the etchant react with oxygen, the liquid turns to a red-brown color and it loses its useful properties. If cooled down after etching, precipitation of silicates in the solution will occur. When preparing the solution, the last ingredient added should be water, (since water addition causes the oxygen sensitivity). All of these make the etchant quite difficult to handle. Table 2.3 shows the etch rates for silicon using EDP.

Table 2.3: Etch rates for silicon using EDP

Formulation	**Temp °C**	**EtchRate (µm/min)**	**(100)/(111) Etch Ratio**	**Masking Films (etch rate)**
Ethyenediamine (750ml) Pyrocatechol (120g) Water (100ml)	115	0.75	35:1	SiO_2 (0.2nm/min) Si_3N_4(0.1nm/min) Au, Cr, Ag, Cu, Ta (negligible)
Ethylene diamine (750ml) Pyrocatechol(120g) Water (240ml)	115	1.25	35:1	SiO_2(0.2nm/min) Si_3N_4 (0.1nm/min) Au, Cr, Ag, Cu, Ta (negligible)

Tetramethyl Ammonium Hydroxide is one of the useful wet etchant chemistries for silicon. The solution is often already present in the clean room, since it is used in many positive photoresist developers. TMAH is nontoxic, not expensive and can be handled easily but the etch rate is slower than EDP and KOH. A concentration above 22wt% is preferable, since lower concentration result in more pronounced roughness on the etch surface. However higher concentration gives a lower etch rate and lower etch ratio (100)/(110).

Etching rate is typically lower on the more densely packed surface than on that of loosely packed surface. The highest atom density is in [111] plane, followed by [100] plane and lastly is in [110] plane. A drawback of wet anisotropic etching is that the microstructure geometry is defined by the internal crystalline structure of the substrate. Consequently, fabricating multiple, interconnected micromechanical structures of free geometry is often difficult or impossible.

Figure 2.3 shows orientation dependent etching of (100)-oriented silicon through patterned silicon dioxide (SiO_2), which acts as a mask. Precise V-grooves, in which the edges are (111) planes at an angle of approximately 55° from the (100) surface, can be realized by the etching. If the etching time is short, or the window in the mask is sufficiently large, U-shaped grooves could also be realized. The width of the bottom surface w, is given by:

$$\begin{aligned} w &= w0 - 2h\coth(55°) \\ w &= w0 - 1.4h \end{aligned} \tag{2.1}$$

where w0 is the width of the window on the wafer surface and h is the etched depth.

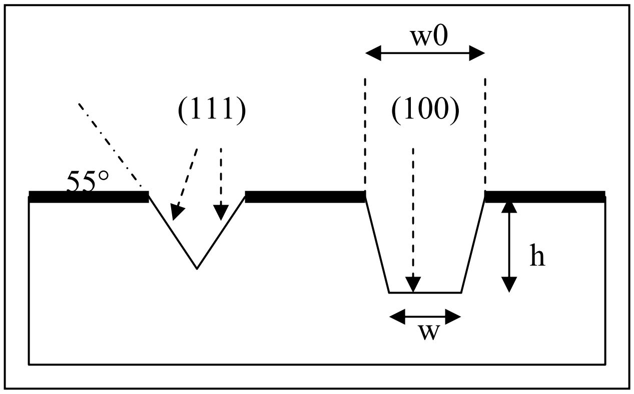

Figure 2.3: Anisotropic etching of (100) silicon