PECVD Silicon Carbide

a promising structural material for surface micromachined devices

Pham Thi Mai Hoa
PECVD Silicon Carbide - a Structural Material for Surface Micromachined Devices

TR 9351

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This book is typeset by the author using $\LaTeX2e$.

Printing: Febodruk BV, Enschede, the Netherlands.

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ISBN: 90-9018856-8
PECVD Silicon Carbide - a Structural Material for Surface Micromachined Devices

PROEFSCHRIFT

ter verkrijging van de graad van doctor
aan de Technische Universiteit Delft,
op gezag van de Rector Magnificus Prof. dr. ir. J.T. Fokkema,
voorzitter van het College voor Promoties,
in het openbaar te verdedigen

op dinsdag 7 december 2004 om 10:30 uur

door

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van International Training Institute for Materials Science, Vietnam
geboren te Hanoi, Vietnam
Dit proefschrift is goedgekeurd door de promotor: Prof. dr. P.M. Sarro

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The work described in this thesis was supported by the Technology Foundation STW.

The work was performed at the Electronic Component, Technology and Materials (ECTM), Delft Institute of Microelectronics and Submicron Technology (DIMES), Delft University of Technology.

Hoa Thi Mai Pham
PECVD Silicon Carbide - a Structural Material for Surface Micromachined Devices
Ph.D. Thesis Delft University of Technology,
with summary in Dutch.

Key words: Silicon carbide material, surface micromachining, post-processing, micro-electromechanical systems.
Contents

1 Introduction
   1.1 The power of a small world ........................................... 1
   1.2 Surface micromachining technology ................................... 2
   1.3 The state of the art of surface micromachining technology ...... 4
   1.4 Motivation and objectives ............................................ 6
   1.5 Organization of this thesis ........................................... 6

2 PECVD silicon carbide for surface micromachining ................. 9
   2.1 Introduction ................................................................ 9
   2.2 Materials for the structural layer ................................... 10
      2.2.1 Semiconducting materials ....................................... 10
      2.2.2 Insulating materials ............................................. 11
      2.2.3 Conducting materials ............................................ 12
   2.3 Silicon carbide: properties and preparations .................... 12
      2.3.1 Properties .......................................................... 12
      2.3.2 Growth and deposition methods .............................. 14
   2.4 The Taguchi method: an experimental design for quality ...... 14
      2.4.1 Design of experiment .......................................... 15
      2.4.2 The Taguchi method ............................................ 15
      2.4.3 Employing the Taguchi method for a PECVD process ....... 16
   2.5 Deposition and etching characteristics of PECVD SiC films .... 17
      2.5.1 Deposition characteristics .................................... 17
      2.5.2 Etching characteristics ....................................... 20
      2.5.3 Effect of doping and post deposition annealing .......... 23
   2.6 Concluding remarks .................................................. 26

3 Structural and mechanical properties of PECVD SiC films ..... 29
   3.1 Introduction ............................................................ 29
   3.2 Structural properties .................................................. 30
3.2.1 As-deposited films ........................................ 30
3.2.2 The effect of in-situ doping .......................... 32
3.2.3 The effect of laser annealing ......................... 34
3.3 Mechanical properties ........................................ 36
3.3.1 Mechanical measurements ............................ 36
3.3.2 Process optimization for low tensile stress films 39
3.3.3 Strain and Young’s modulus ......................... 46
3.4 Concluding remarks ........................................ 47

4 Optical and electrical properties of PECVD SiC films .... 49
4.1 Introduction ................................................ 49
4.2 Optical properties ........................................ 50
4.2.1 Spectroscopic ellipsometry of thin films ......... 50
4.2.2 Theoretical models for determining optical parameters 52
4.2.3 Experimental ........................................ 55
4.2.4 Results and discussions .............................. 55
4.3 Electrical properties ....................................... 64
4.3.1 Test structures ........................................ 64
4.3.2 Experimental ........................................ 67
4.3.3 Results and discussions .............................. 68
4.4 Concluding remarks ....................................... 73

5 All-dry post-processing surface micromachining module . 75
5.1 Introduction ................................................ 75
5.2 Materials for sacrificial layers .......................... 76
5.2.1 Insulating materials .................................. 76
5.2.2 Semiconducting materials ........................... 77
5.2.3 Conducting materials ................................ 78
5.3 The stiction problem ...................................... 78
5.3.1 Adhesion forces ...................................... 79
5.3.2 Anti-stiction methods ................................ 82
5.4 Polyimide as a sacrificial layer ......................... 86
5.4.1 Preparation of polyimide ............................ 86
5.4.2 Dry etching of the polyimide ...................... 87
5.5 An all-dry post-processing surface micromachining module ... 89
5.5.1 A surface micromachining module ................ 90
5.5.2 Realization of microstructures .................... 90
5.6 Concluding remarks ....................................... 91
6 Applications

6.1 Introduction .................................................. 93
6.2 Surface micromachined PECVD SiC microstructures .... 94
  6.2.1 Electrostatic switch ...................................... 94
  6.2.2 Pressure sensor ........................................... 96
  6.2.3 Vertical accelerometer .................................... 99
6.3 Other possibilities of PECVD SiC films ................. 102
  6.3.1 Mach Zehnder interferometer .......................... 102
  6.3.2 Humidity sensor ........................................ 104
6.4 Concluding remarks ......................................... 107

7 Conclusions and future work ................................. 109

7.1 Conclusions .................................................. 109
7.2 Future work .................................................. 110

A The Taguchi method ........................................... 113
A.1 The Taguchi table ........................................... 113
A.2 ANOVA ......................................................... 113

B Process flow for test structures and devices ............ 121
B.1 van der Pauw structure preparation ...................... 121
B.2 MIM structure preparation ................................ 122
B.3 MIS structure preparation ................................ 123
B.4 Polyimide preparation ....................................... 124
B.5 All-dry post-processing .................................... 124
B.6 Switch preparation .......................................... 125
B.7 Pressure sensor preparation ............................... 126
B.8 Accelerometer preparation .................................. 127
B.9 Mach Zehnder interferometer ............................. 127
B.10 Humidity sensor preparation .............................. 128

Bibliography ..................................................... 129

Summary ........................................................ 141

Samenvatting ...................................................... 145

Publications ...................................................... 149

Acknowledgements ................................................ 155
Chapter 1

Introduction

1.1 The power of a small world

The ability to manipulate objects invisible to the naked eye has transformed the way we live. Nowhere is this more evident than in the medical world, where the control and make-up of genes just a few hundred atoms long is considered vital to our understanding of the human body and illnesses. Another example is a robot defined by a set of sensors, computers and actuators. Nowadays, microrobots are quite effective, and scientists have achieved "complete self-contained working systems that sense, think, act and communicate, albeit simply". Nevertheless, there is still a fascinating dream of cell-sized microrobot (nanorobot), which is a flexible system and can be easily adapted to a particular problem. Clearly, making technology work at a smaller and smaller scale is getting great attention [1]. Advances in material science and processing in microelectronics are the key toward this goal.

"Smaller, faster and more efficient" is the maxim of the microelectronics industry as it strives towards further miniaturization of electronic components, thanks to the continuous advances in silicon integrated circuit (IC) technology in terms of both processing and equipment. Along with electronics, the sensors and actuators produced by silicon IC processes are also miniaturized. This revolution is having a tremendous impact on the Microsystems technology for the fields of sensing, computing and wireless network communication.

Microsensors and microactuators integrated with microelectronics are often known as intelligent (or smart) sensors and actuators or as microelectromechanical systems (MEMS). Over the last couple of decades, these systems have been developed to radically transform their scale, performance and cost by exploiting batch-fabrication techniques and other achievements in the IC
industry. Specifically, MEMS technology has made it possible to reduce the size of many types of sensors, actuators and systems by several orders of magnitude, while improving device performance [2].

Silicon possesses excellent mechanical properties, making it an ideal material for micromachining [3]. Integration of MEMS technology with on-chip electronics is the next logical step in the Si revolution, not only because of the similarity in processing, packaging, and applications but also for the expensive mass-production facilities already available in the IC industry [4].

There is a number of processes and techniques relevant to MEMS technology that can be used to produce three-dimensional (3D) microstructures. Almost all the processes fall into either bulk micromachining or surface micromachining techniques. Table 1.1 shows some major characteristics of structures fabricated in these two technologies. The vertical dimensions of bulk micromachined structures are usually determined by the thickness of the wafer used, whereas those of surface micromachining come from the practical layer thicknesses that can be deposited.

Table 1.1: Comparison between bulk and surface micromachining techniques [5].

<table>
<thead>
<tr>
<th></th>
<th>Bulk</th>
<th>Surface</th>
</tr>
</thead>
<tbody>
<tr>
<td>Processing complexity</td>
<td>medium</td>
<td>high</td>
</tr>
<tr>
<td>Lateral dimensions</td>
<td>3-5mm</td>
<td>100-500µm</td>
</tr>
<tr>
<td>Vertical dimensions</td>
<td>100-500µm</td>
<td>0.5-2µm</td>
</tr>
<tr>
<td>Planar geometry</td>
<td>rectangular</td>
<td>unrestricted</td>
</tr>
</tbody>
</table>

Surface micromachining technology has advantages over bulk micromachining for integrating MEMS technology with on-chip electronics because fabricated structures can be smaller and easily integrated. One of the main advantages of surface micromachining is that a slightly modified conventional IC process can be used for the realization of the MEMS device [6, 7]. The next section presents a brief description of potentials and limitations of conventional surface micromachining techniques.

1.2 Surface micromachining technology

Surface micromachining involves two basic types of layers. The first is known as the sacrificial layer, which is removed during processing and therefore does
not exist in the final device. The second is the structural layer, which forms the mechanical structure. A simple conventional surface micromachining process is shown in figure 1.1. First a sacrificial layer is formed and patterned, followed by a similar process for a structural layer. Finally the sacrificial layer is removed by etching to leave a free-standing structure.

![Diagram of micromachining process](image)

Figure 1.1: The basic surface micromachining process [8].

Many of the microfabrication techniques, e.g. photolithography, thermal oxidation, low pressure chemical vapor deposition (LPCVD), plasma enhanced chemical vapor deposition (PECVD), and wet etching, reactive ion etching (RIE) used in surface micromachining technology have been borrowed from the IC industry. Although silicon is a typical material for surface micromachining, various materials such as piezoelectric films (e.g. PZT), magnetic films (e.g. Ni, Fe, Co and rare earth alloys), and high-temperature materials (e.g. silicon carbide, ceramics) that are not traditionally used by the IC industry are used as sacrificial and structural layers.

The main challenge in surface micromachining is to achieve a free-standing structure on small scale. There are three crucial issues

- Control of stress and stress gradients in the structural layer to avoid bending or buckling of the released microstructure.
- High selectivity of the sacrificial layer etchant to the structural layer.
- Avoidance of stiction of the released microstructure to the substrate.

The main features of the surface micromachining technology are the small dimensions of the microstructures and the opportunity to integrate micromechanics and microelectronics on the same chip. To integrate surface micromachining with electronics, a number of issues have to be considered in terms
of materials and processing compatibility. A major consideration in the
development of a process is the thermal budget, as any addition temperature
step can have a significant influence on the properties of the device. Another
important consideration is the protection of the electronics during the etching
of the sacrificial and structural layers.

1.3 The state of the art of surface micromachining
technology

In 1985, Barth suggested the term “surface micromachining” when using a
sacrificial layer to form thin film microstructures [9]. However, this concept
was already demonstrated in the mid-1960s when Nathason et al. [10] used
a metallic cantilever beam as a “resonant gate” for a field effect transistor
(FET). Unfortunately, this work did not receive much attention at the time.

In the early 1980s, a surface micromachining technique was first success-
fully applied to fabricate polysilicon microstructures such as beams and bridges
using silicon dioxide as a sacrificial layer [11]. Polysilicon surface micromach-
ing was quickly recognized as a promising technology and employed at both
academic and industrial laboratories. Toward the latter half of the 1980s, re-
searchers had demonstrated micromechanisms and electrostatic micromotors
based on polycrystalline surface micromachining. The control of mechanical
properties of polysilicon has been studied extensively and is now relatively
well understood [12].

Nowadays, surface micromachining technology plays a very important role
in the significant development in the field of MEMS. This exciting area has
found application in many fields, including aerospace, aeronautics, military,
civil engineering, biomedical, information technology, consumer electronics
and automotive industry. A number of new materials and techniques have
been proposed and studied in order to overcome the limitations of surface
micromachining, especially the stiction problem. Furthermore, combinations
between surface micromachining with other technologies such as bulk micro-
machining (wet and dry), Lithographie Galvanof ormung Abformung (LIGA),
and laser cutting have realized many new MEMS devices [13, 14].

Different sensors, actuators and smart devices have been developed and
demonstrated for specific applications. In the sensor field, pressure sensors
with new characteristics for new applications are still being developed. For in-
stance, Melvas et al. [15] presented an entirely surface micromachined resonant
beam pressure sensor that enables high-pressure sensitivity and a miniature
chip size, essential for catheter mounted intravascular blood pressure sensors.
One of the successful commercial applications is the accelerometer for air bags. A novel microaccelerometer with high device sensitivity, low noise, low damping, low cross-axis sensitivity, low-temperature sensitivity, and potentially good long-term stability has been proposed by Yazdi and Najafi, along with the development of a new combined surface and bulk microfabrication process [16]. Another example is a magnetic field sensor based on an alternative approach using a micromechanical resonator incorporating a magnetic material [17].

In addition to sensors, actuators have been fabricated, although they have not received equal attention. A microgripper is a MEMS device that uses different microactuators, such as electrostatic comb-drives, piezoelectric stacks, shape memory alloy, or thermal actuators. Recently, polymer microgrippers that can handle microparts or manipulate cells have been fabricated using surface micromachining with SU-8 photoresists as the structural material and silicon as the sacrificial material [18]. Micromirrors have shown their potential application in the fields of optical scanning, projection display, optical switching and optical telecommunications. Surface micromachining combined with flip chip bonding has been used to realize a micromirror device that can improve the linearity of typical electrostatic-driving micromirror devices [19].

Another example of surface micromachined systems is an inductively coupled plasma generator, one type of electrodeless discharge that is now widely used in microfabrication processes [20]. This miniaturized device is needed for several MEMS applications, including ionizers for mass spectrometers, thrusters, plasma displays, and atomic emission spectroscopy.

Technologies that merge different surface micromachining processes with various electronic processes have been an active topic of research. Several processes for integrating MEMS technology with on-chip electronics have recently been presented in literature. Bustillo et al. [21] used tungsten metallization to solve the thermal budget problem. In the process used by Kuehnel and Sherman [22], aluminum metallization is performed after the sacrificial etching and subsequently the wafer is covered with an oxynitride layer. Drienhuizen et al. [23] developed a compatible post-processing surface micromachining process using a resist protective layer during sacrificial etching. A similar process has been developed by Fisher et al. [24].

In short, the current trend is to employ new materials and processes in realizing novel devices. Research in this field thus focuses on integrating different surface micromachining processes with microelectronic processes.
1.4 Motivation and objectives

Integrating surface micromachining into standard processing can complicate the process, reduce yield, and thus increase cost. It is important to establish a strategy determining how and when the surface micromachined devices can be inserted into the standard process. As an example, if the micromachining is performed early in the processing the additional thermal steps may adversely affect the mechanical structures [8].

In order to avoid these problems, post-processing surface micromachining is a flexible and economically attractive approach.

In post-processing surface micromachining, the temperature must be maintained below 400°C as aluminum metallization is used in most conventional IC processes. It is therefore necessary to develop micromachining processes which either use existing or additional layers that can be deposited and patterned at a temperature lower than 400°C. Materials prepared by PECVD techniques, as well as certain metals and polyimides meet this criterion. For each of the materials to be used, there are two important considerations: their compatibility with IC processes, and the specific properties of this material.

Moreover, in designing microfabricated devices, it is important to be aware that the properties of thin film materials are often significantly different from their bulk form. Much of this disparity arises from the difference in the processes used to produce thin film materials and bulk materials. A number of microstructures have revealed that properties of thin film material can vary tremendously from film to film without a careful process control. Any high precision and high reliability application requires that significant effort be directed toward quantifying precisely the material properties of the films being employed.

1.5 Organization of this thesis

In this thesis, new materials and their applicability for post-processing surface micromachining to integrate sensors and actuators with on-chip electronics are investigated.

Chapter 2 gives a short overview of materials used as structural layers. In particular, SiC is introduced as an alternative to existing materials with several interesting properties, including high mechanical strength, high thermal conductivity, remarkable inertness in several liquid electrolytes and the ability to operate at high temperature. A detailed design of experiments aiming at optimizing the PECVD SiC layers as structural material is presented.
The effect of deposition parameters, in-situ doping (p- and n-type) and post-deposition annealing (thermal annealing and laser annealing) on deposition and etching characteristics of SiC films is investigated.

In chapter 3, structural properties of PECVD SiC are studied, including the effect of doping and laser annealing. By combining the design of experiments with a mathematical technique, an empirical model is derived to control the stress of SiC films. Furthermore, the effect of boron and phosphorus doping and subsequent thermal annealing on the stress of SiC films is studied. Finally, the strain and Young’s modulus of a low stress SiC film are calculated.

In chapter 4, the effect of deposition parameters on the optical and electrical properties of PECVD SiC thin films is investigated. By applying the Tauc model, the Wemple and DiDominico model, and the Spitzer and Fan model, important optical constants of SiC films are calculated. Using the van der Pauw, metal-insulator-metal (MIM), and metal-insulator-semiconductor (MIS) structures, the conduction mechanisms in SiC films are studied. The dielectric constant, the breakdown voltage, leakage current density and flat band voltage of SiC thin films are calculated as well.

In chapter 5, an overview of materials used as sacrificial layers in surface micromachining is given. Mechanisms causing stiction in the releasing step of the microstructures are reviewed, and frequently used prevention approaches are described. Subsequently, a novel all-dry process using SiC as a structural layer and polyimide as a sacrificial layer is presented.

Chapter 6 presents several microstructures using SiC films. Firstly, we discuss the characterization of three types of surface micromachined devices, fabricated using low tensile stress PECVD SiC films as a structural layer, namely switches, accelerometers, and pressure sensors. Other applications of SiC, namely porous SiC layers for humidity sensors and SiC layers for Mach Zehnder interferometers, are also discussed.

Finally, chapter 7 presents conclusions and suggestions for future research.
Chapter 2

PECVD silicon carbide for surface micromachining

2.1 Introduction

The structural (or mechanical) layer is a crucial component of a surface micromachined device. One needs to study the specific mechanical, optical, electrical and thermal properties desired of this layer, which are dictated by its application fields or environmental constraints. Although several insulators, semiconductors and conductors have been investigated as structural layers, generally most of them cannot be used in harsh environments such as high temperature or corrosive media.

Silicon carbide (SiC), a new practical material for Microsystems, has recently received increasing attention [25]. A SiC film in either crystalline or amorphous states possesses many interesting properties, including a high mechanical strength, high thermal conductivity, an ability to operate at high temperature, low friction and wear resistance, and remarkable chemical inertia in several liquid electrolytes. These properties make it particularly suited, both as a structural and as a coating layer, for MEMS applications in harsh environments [26, 27, 28].

As mentioned in the previous chapter, to realize smart micromechanical devices it is essential that the surface micromachining technology is compatible with conventional IC processing. A SiC film prepared by the PECVD technique provides an attractive possibility for a post-process surface micromachining approach, because the deposition and patterning techniques of this material operate at temperature below 400°C, the maximum temperature allowed for additional steps after a conventional IC process.
In order to acquire a high-quality SiC film for a particular application, we have to refine the PECVD process. It is important to control the film properties by varying the deposition parameters, examining their effects on the results, and subsequently optimizing their values. However, one faces the general problem of a large number of deposition parameters that strongly affect the properties of the thin film. An effective and economical approach to overcome this problem is the Taguchi method, which provides information about the process when the parameters are varied simultaneously; thus the interactions between parameters are also considered [29, 30]. Furthermore, this method enables one to reduce the number of experiments performed, saving a tremendous amount of time.

Section 2.2 presents a brief overview of materials commonly used for structural layers in surface micromachining. Section 2.3 and section 2.4 summarized general properties and the preparation technology of SiC, and show how to use the Taguchi method to design of experiments aimed at optimizing the PECVD SiC layers. Deposition and etching characteristics of these layers and their relations to the deposition parameters are described in section 2.5. Finally, section 2.6 presents the effect of in-situ doping and post-deposition annealing (both thermal annealing and laser annealing) on the properties of SiC films.

### 2.2 Materials for the structural layer

Structural materials must possess the desired electrical and mechanical properties for the application envisioned. There are two main requirements for a structural material. Firstly, the structural layer should have low tensile stress to ensure a flat structure after releasing. Secondly, it must be resistant to the etchant used to remove the sacrificial layer [8].

There is a wide range of micromechanical layers available. Generally, Si-based materials or materials compatible with conventional IC processes are preferred for the integration of surface micromachining techniques with on-chip electronics. The following is a brief overview of materials most frequently used for the structural layer in surface micromachining.

#### 2.2.1 Semiconducting materials

- Polycrystalline silicon (Poly-Si): Poly-Si is widely used, not only in microelectronics but also in micromechanical devices. A major factor contributing to the large use of poly-Si is the mature infrastructure for
depositing, patterning and etching of poly-Si established by the IC industry. So far, poly-Si integrated microdevices have been playing a key role in developing the MEMS and circuit building blocks for inertial measurements [31, 32, 33]. Doped poly-Si films have also been considered as structural layers for surface micromachined devices [34, 35]. These films are usually required for applications that need a high conductivity level to act as an electrode. In [36], the authors studied the residual stress as a function of the doping concentration and found no significant effect on the Young’s modulus for both types of doping poly-Si layers.

- Germanium (Ge): The advantages of using Ge as a structural layer over other materials commonly used are its excellent etching selectivity in both gas and liquid phase, and its low deposition temperature that potentially allows the use of Ge for post-processing in a conventional IC process. Similar to Si, Ge can be used to realize a variety of sensors, such as Ge microthermistors [37].

- Silicon Germanium (SiGe): SiGe has been reported as a suitable material for microelectronics applications requiring a low thermal budget. Since a low-stress SiGe layer can be achieved at a low process temperature, surface micromachined SiGe structures can be fabricated that are compatible with conventional IC processes. Bolometers and thermopiles using SiGe as structural layers demonstrate superior thermoelectric properties and are being transferred to industrial use [38, 39].

2.2.2 Insulating materials

- Silicon nitride (SiN): both SiN films prepared by PECVD and LPCVD techniques are found in a wide range of applications in microelectronic technology, mostly as an insulator or a surface passivation layer. In the microsystem world, it is often employed as a thin membrane structure in devices such as interferometers, thermal IR detectors, and Fabry-Perot cavities, where both mechanical and optical properties of the material are important [40, 41, 42].

- Silicon oxynitride (SiON): A SiON film is a promising material for MEMS and microoptoelectromechanical systems (MOEMS). It is advantageous when compared to SiO and SiN due to the possibility of controlling their chemical composition and their structural, optical and mechanical properties by an appropriate choice of deposition parameters [43, 44].
2.2.3 Conducting materials

- Metals: A variety of metals such as nickel (Ni), gold (Au), copper (Cu) and palladium (Pd) have been used in micromachined structures. Films of these metals can be prepared by sputtering or evaporation at low temperature (< 400°C), thus they are suited for post-process surface micromachining. An advantage of using metals as structural layers is that a number of materials can be used as a sacrificial layer due to their high selectivity in both dry and wet etching. Although metals have low mechanical strength, they also have low resistivity. Therefore attempts have been made to combine them with other materials to create the desired structural layer. A MEMS process has been reported using aluminum (Al) as a structural layer for fabricating an electrostatic actuator, compatible with the future use of underlying, pre-fabricated CMOS or BiCMOS circuits [45]. Metals are especially attractive for the fabrication of microchannels, because they produce large cross-sectional areas, achieve high heat transfer rates through a metallic wall, allow the possibility of resistive heating of fluids, and achieve precise definition of the inner channel dimension and volume [46].

2.3 Silicon carbide: properties and preparations

Recent developments in SiC deposition techniques, especially the improved control of material properties, have resulted in a number of SiC MEMS devices and structures [25]. This section discusses general properties of SiC materials and its preparation.

2.3.1 Properties

Figure 2.1 shows the zincblende and hexagonal bonding of carbon (C) atoms with the Si neighbors in SiC molecules. The Si-C bonds are shorter (1.88Å) than the Si-Si bonds (2.35Å) [47]. Crystalline SiC (c-SiC) occurs in many different structures that exist in over 250 polytypes. Despite this large number, currently only three are technologically relevant: 3C-SiC, 6H-SiC and 4H-SiC [48]. Amorphous SiC, referred to a-SiC, is characterized by a network of Si-C bonds with high concentrations of Si-H and C-H bonds, dangling bonds and hydrogen trapped in voids [49]. The average binding energy of Si and C atoms in an a-SiC layer is considerably lower than that in c-SiC mainly due to the incorporated hydrogen [50].
Table 2.1: Comparison of general properties between SiC and other semiconductors.

<table>
<thead>
<tr>
<th>Properties</th>
<th>3C-SiC</th>
<th>6H-SiC</th>
<th>Si</th>
<th>GaAs</th>
<th>Diam.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bandgap (eV)</td>
<td>2.2</td>
<td>2.9</td>
<td>1.1</td>
<td>1.4</td>
<td>5.5</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>1800</td>
<td>1800</td>
<td>1420</td>
<td>1240</td>
<td>-</td>
</tr>
<tr>
<td>Young modulus (GPa)</td>
<td>448</td>
<td>448</td>
<td>75</td>
<td>190</td>
<td>1035</td>
</tr>
<tr>
<td>Therm. coef. (×10^{-6}K^{-1})</td>
<td>3.8</td>
<td>4.2</td>
<td>6.9</td>
<td>2.6</td>
<td>-</td>
</tr>
<tr>
<td>Elect. mobility (cm²/Vs)</td>
<td>40</td>
<td>40</td>
<td>600</td>
<td>400</td>
<td>1600</td>
</tr>
<tr>
<td>Break. voltage (10V/cm)</td>
<td>4.0</td>
<td>4.0</td>
<td>0.3</td>
<td>0.4</td>
<td>10</td>
</tr>
<tr>
<td>Therm. cond. (W/cmK)</td>
<td>5.0</td>
<td>5.0</td>
<td>1.5</td>
<td>0.5</td>
<td>20</td>
</tr>
<tr>
<td>Sat. velocity (10^7cm/s)</td>
<td>2.5</td>
<td>2.0</td>
<td>1.0</td>
<td>2.0</td>
<td>2.7</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>9.7</td>
<td>10</td>
<td>11.8</td>
<td>12.8</td>
<td>5.5</td>
</tr>
</tbody>
</table>

Table 2.1 compares c-SiC and other semiconductors used in microelectronics. Compared to Si and GaAs, SiC demonstrates higher thermal conductivity, higher chemical inertness and radiation resistance, which increases its potential for use in sensors operating in adverse environments. Such applications are in instrumentation and control of nuclear power systems, which require high-temperature transducers capable of operating in radiation environments. In comparison to diamond, attractive features of SiC are that it can be doped both p-type and n-type and it allows growth of a natural oxide on its surface.
2.3.2 Growth and deposition methods

Various methods have been used to produce SiC bulk and SiC films on different substrates. For SiC bulk crystals, physical vapor transport (PVT) using a seed, also called the modified-Lely method or seeded sublimation growth, is the only growth technology used at present [51]. For SiC film preparation, chemical vapor deposition (CVD) methods are the main technique used. They produce high-quality films on a large area, which are suitable for mass production [52].

In a CVD process to grow SiC films, numerous sources of Si and C molecules have been studied extensively [53]. Silane (SiH₄) is a common Si source. Various hydrocarbons have been used as C sources. Propane (C₃H₈) is the most popular because of its association with the first successful demonstration of large-area epitaxial SiC on a Si substrate, while methane (CH₄), ethylene (C₂H₄) and acetylene (C₂H₂) have been used less extensively [53]. CH₄ has our interest because of the increased purity available from commercial sources compared to that of C₃H₈, despite that its larger thermal stability results in a smaller C source cracking efficiency.

There are two main CVD methods, namely LPCVD and PECVD; both are essential in bulk micromachining and even more so in surface micromachining [54]. In principle, LPCVD and PECVD processes are both carried out at low pressure. The former generally operates at a temperature ranging from 800°C to 1000°C, and the latter at a lower temperature (< 400°C) and it needs auxiliary energy sources such as RF generators, light sources, or microwave sources to enhance the chemical reaction by supplying radicals from plasma. Due to its lower operating temperature, the PECVD technique is more suitable for post-processing surface micromachining.

The advantage of SiC films prepared by a PECVD technique on a Si substrate is that by varying the deposition parameters material properties can be optimized while the compatibility with conventional IC processes is maintained. One of our main objectives is to refine the PECVD process to prepare high-quality SiC layers for specific MEMS applications using post-process surface micromachining techniques.

2.4 The Taguchi method: an experimental design for quality

In order to optimize the PECVD process for SiC film preparation, a careful evaluation of the optimization problem and a proper use of design of experiment are necessary. These topics will be discussed in this section.
2.4.1 Design of experiment

Traditionally, the effect of process parameters on film properties is examined by varying one separate parameter at a time while keeping the other parameters constant. However, this approach does not necessarily lead to a real optimum. It provides no information about what happens when the factors are varied simultaneously, i.e., it ignores the interactions between factors, leading to isolated, unconnected experiments. As a consequence, this approach requires a large number of experiments to achieve a reasonable result.

To overcome this problem, one needs a design of experiment (DoE). It provides a systematic approach for optimization. It offers a means to study a system influenced by more than one parameter and gives a better estimation of the variability and noise of the system; hence, it increases the optimality of the results. Together with a thorough statistical modeling and analysis, it yields useful and precise information about the process, and helps determine the hidden relationships between process parameters and the outcome in a comprehensive manner [55]. Furthermore, DoE naturally minimizes the number of depositions and tests required. The savings in time and money are considerable when a careful design taking into account only the most useful combinations is employed.

The choice of a DoE depends on the objective of the experiment and the number of factors to be investigated. Important methods commonly used in DoE are Full Factorial Design [56], $2^{(k-p)}$ Fractional Factorial Designs [56], $3^{(k-p)}$ Box-Berken and Mixed two- and three-level Fractional Designs [56], and the Taguchi method [29, 30]. The common goal of these methods is to identify the optimum settings for the different factors that affect the process outcome.

2.4.2 The Taguchi method

The goal of a Taguchi experimental design is to identify an optimal setting for all the design parameters. The method enables one to simplify the calculations, saving a large amount of time in data analysis. Unlike other methods, the Taguchi method considers the interaction between control and noise factors through evaluation of the signal to noise ratio.

According to the Taguchi method, orthogonal arrays are used to design the experiments. There are many standard orthogonal arrays available, each of which is meant for a specific number of independent design variables and levels. They are indicated as $L_{x}a^{y}$, where $x$, $a$ and $y$ are the number of experiments, variables and levels, respectively. Each array assumes that there
Table 2.2: The orthogonal array table designated for four factors at three levels \((L_3^{3^4})\).

<table>
<thead>
<tr>
<th>Run</th>
<th>factor 1</th>
<th>factor 2</th>
<th>factor 3</th>
<th>factor 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
<td>-1</td>
</tr>
<tr>
<td>2</td>
<td>-1</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>-1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>-1</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>0</td>
<td>1</td>
<td>-1</td>
</tr>
<tr>
<td>6</td>
<td>0</td>
<td>1</td>
<td>-1</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>1</td>
<td>-1</td>
<td>1</td>
<td>0</td>
</tr>
<tr>
<td>8</td>
<td>1</td>
<td>0</td>
<td>-1</td>
<td>1</td>
</tr>
<tr>
<td>9</td>
<td>1</td>
<td>1</td>
<td>0</td>
<td>-1</td>
</tr>
</tbody>
</table>

is no interaction between any two factors.

Properties of an orthogonal array are:

- The vertical column under each independent variable has a special combination of level settings. All level settings occurs an equal number of times. This is called the balancing property of orthogonal arrays.

- All the level values of independent variables are used for conducting the experiments.

- The sequence of level values for conducting experiments will not be changed because the array of each factor columns is mutually orthogonal to any other column of level values. The inner product between two column vectors is zero.

As an example, an orthogonal array for four factors at three levels is shown in table 2.2. In this case, only nine experimental runs are required. The factor level codings of -1, 0 and 1 represent the low, central and upper level of the variables, respectively.

2.4.3 Employing the Taguchi method for a PECVD process

The Taguchi method has been employed here to study the influence of deposition parameters on the properties of the resulting SiC film. We aimed
to identify all deposition parameters that can influence the properties of SiC films.

The basic steps of the Taguchi method for depositing a PECVD thin film for a specific application are summarized in the following

1. Select the most significant parameters that cause variation of the PECVD process. In our system, five parameters with three levels have been chosen. These parameters are independently controlled during the deposition process. The selected deposition parameters, along with their ranges, are given in table 2.3.

2. Run the deposition processes under the experimental conditions dictated by the chosen orthogonal array and parameter levels. The array has five columns and specifies 27 experimental runs. The assignment of the deposition parameters to the $L_{27}3^5$ orthogonal array is given in appendix A.1.

3. Analyze the data. An analysis of variance (ANOVA) table is generated to determine the statistical significance of the parameters. Response graphs are plotted to determine the preferred level for each parameter. The calculation is shown in appendix A.2.

4. Verify the model obtained by contrasting the outcomes of the experiment with new sets of parameter value and those predicted by the model.

2.5 Deposition and etching characteristics of PECVD SiC films

In this section, we investigate the effect of deposition parameters on properties of PECVD SiC films using experimental design and statistical analysis. The influence of doping and post-deposition annealing on properties of the films will also be reported.

2.5.1 Deposition characteristics

In plasma enhanced deposition of thin films, many reactions are involved, both in the plasma phase and on the substrate surface. Therefore, to obtain a desired film composition and microstructure, one needs to understand the mechanism that governs the film formation.
Formation mechanism

The reaction mechanism involved in PECVD of thin films is not well understood. In principle, it obeys the fundamental reaction mechanism of CVD. This is a process where one or more gaseous species react on a solid surface and one of the reaction products is a solid phase material [54]. Figure 2.2 shows the reaction mechanism in film formation in CVD [57]. The following steps occur in every CVD reaction

- Transport of the reacting gaseous species onto the surface.
- Adsorption or chemisorption of the species on the surface.
- Heterogeneous surface reaction catalyzed by the surface.
- Desorption of gaseous reaction products.
- Transport of reaction products away from the surface.

![Diagram of CVD process](image)

Figure 2.2: Formation mechanism of a CVD process.

The following mechanism for SiC deposition by PECVD is suggested in [58]. The dissociation of SiH$_4$ in a discharge essentially generates SiH$_x$ radicals ($x = 2,3$)

$$\text{SiH}_4 \rightarrow \text{SiH}_x + \frac{(4 - x)}{2} \text{H}_2$$
In plasma, either the direct dissociation of CH₄ or the reaction with an H atom can form CH₃ radicals

\[ \text{CH}_4 \rightarrow \text{CH}_3 + \text{H} \]

\[ \text{H} + \text{CH}_4 \rightarrow \text{H}_2 + \text{CH}_3 \]

SiHₓ radicals may react with CH₃ radicals in two paths (i) a gas phase reaction between SiH₃ and CH₃ radicals to form an intermediate product, most probably CH₃SiH or H₂Si=CH₂ resulting in SiC.

\[ \text{SiH}_3 + \text{CH}_3 \rightarrow \text{CH}_3\text{SiH} + \text{H}_2 \]

\[ \text{CH}_3\text{SiH} \rightarrow \text{H}_2\text{Si} = \text{CH}_2 \rightarrow \text{SiC} + 2\text{H}_2 \]

and (ii) a reaction of the gaseous SiHₓ with CH₃ adsorbed on the surface to give SiC

\[ \text{SiH}_x + \text{CH}_3 \rightarrow \text{SiC} + \frac{3+x}{2}\text{H}_2 \]

**Experimental**

SiC films were deposited in a commercial type PECVD system, the Novellus Concept One system. This is a multi-station, sequential deposition reactor, which allows process optimization while maintaining a high throughput. SiH₄ gas was used as the Si source and CH₄ as the C source. All reaction gases were used in diluted form (i.e., in Ar) for safety purposes.

Si wafers with a 100nm thermal SiO₂ layer were used as a substrate. The wafers were cleaned in HNO₃ 100% and rinsed thoroughly in de-ionized water prior to loading into the reactor. The deposition parameters with their ranges and values at three levels are summarized in table 2.3.

In our experiments, we kept the CH₄ flow rate constant at 3000(sccm). The list of experiments carried out following the orthogonal array design can be seen in appendix A.1. To eliminate any effect on the properties related to the equipment, we carried out the experiments in a random order.

A surface profiler (DEKTAK 8, Veeco) and a spectroscopic ellipsometer (SOPRA-ES4T) were used to measure the thickness of SiC films.
Table 2.3: Process parameters with their ranges and values at three levels.

<table>
<thead>
<tr>
<th>Process parameters</th>
<th>Symbol</th>
<th>Level 1</th>
<th>Level 2</th>
<th>Level 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>A</td>
<td>300</td>
<td>350</td>
<td>400</td>
</tr>
<tr>
<td>Pressure (Torr)</td>
<td>B</td>
<td>1.5</td>
<td>2.0</td>
<td>2.5</td>
</tr>
<tr>
<td>SiH₄ flow rate (sccm)</td>
<td>C</td>
<td>150</td>
<td>200</td>
<td>250</td>
</tr>
<tr>
<td>High Frequency (W)</td>
<td>D</td>
<td>250</td>
<td>500</td>
<td>750</td>
</tr>
<tr>
<td>Low Frequency (W)</td>
<td>E</td>
<td>250</td>
<td>500</td>
<td>750</td>
</tr>
</tbody>
</table>

Results and discussions

We investigate the influence of the deposition parameters on the deposition rate of SiC films. The deposition rate is in the range from 40nm/min. to 100nm/min., see in appendix A.1. Figure 2.3 shows that this rate depends on the deposition parameters. It increases as the pressure, SiH₄ gas flow rate, LF component and power increase, while the temperature decreases. The SiH₄ gas flow rate plays the most important role in increasing the deposition rate while the HF component has almost no effect. The contribution of each deposition parameter can be seen in appendix A.2.

![Deposition rate vs. parameters](image)

Figure 2.3: Effect of deposition parameters on the deposition rate of SiC films.

2.5.2 Etching characteristics

The deposited SiC films must be patterned to define the microstructure [59, 60]. Furthermore, the etching characteristic of the PECVD SiC films in gas or liquid environments must also be examined to guarantee the device is suitable for operation in a harsh environment.
Both wet etching and dry etching have been studied. Previous results on wet etching of PECVD SiC indicate that SiC is resistant to many wet chemical etchants [61]. As for dry etching, most investigations have been performed using reactive ion etching (RIE) or plasma etching (PE) modes [59]. Figure 2.4 schematically shows four basic plasma etching processes. RIE is a widely used technique for pattern transfer, since it provides easily controllable etch rates, preservation of stoichiometry, selectivity, and a smooth and residue-free surface [62].

**Plasma etching mechanism**

In general, plasma based dry etching either in fluorinated or chlorinated compounds (NF₃, CF₄, SF₆, CHF₃, CCl₄ and mixture with O₂) are used to pattern PECVD SiC films [50, 59]. The influence of the addition of O₂ to the gas used has been investigated [62]. Adding O₂ to a CF₄ gas flow yields more F atoms available for the etching reactions. In fact, with a low O₂ percentage, no considerable SiC removal is observed. Moreover, Padiath et al. [63] reported that the etch rate was almost constant up to 30% O₂ in the etchant mixture and it decreased when O₂ in the feed gas was increased beyond 30% gradually. An understanding of the etching reactions, on an atomic scale, requires information about [64]

- The types of gaseous species capable of reacting with surfaces,
- The volatile products which are formed,
- The processes that lead reactants to products.
The reactive ion etching mechanism of SiC films is as follows. Dissociation of CF$_4$ and SF$_6$ leads to free F atoms, and CF$_x$ (x ≤ 3) and SF$_y$ (y ≤ 5) fluorinated fragments. The dissociation reactions and the Si etch reaction are given by

$$\text{CF}_4 + \text{O}_2 \rightarrow \text{CF}_x + \text{F} + \text{O} + (\text{CO} + \text{CO}_2)$$

$$\text{SF}_6 + \text{O}_2 \rightarrow \text{S} + 6\text{F} + 2\text{O}$$

$$\text{Si} + 4\text{F} \rightarrow \text{SiF}_4$$

$$\text{C} + 2\text{O} \rightarrow \text{CO}_2$$

The etch product SiF$_4$, CO$_2$ are volatile and easily pumped away, thus completing the etching process.

**Experimental**

The dry etching experiments were carried out in an Alcatel GIR 300 fluorine etcher system. A pressure of 500mbar and a power of 60W were set up. A mixture of CF$_4$:SF$_6$:O$_2 = 70:10:10$ gases has been used to anisotropically pattern SiC layers. Both CF$_4$ and SF$_6$ were used in this experiment because they are stable, relatively easy to handle, non-corrosive and of low toxicity [62]. Moreover, experimentally the addition of SF$_6$ yields better performance than using pure CF$_4$ plasma [65]. Photoresists AZ3012 and AZ3017 have been used as a mask for etching PECVD SiC with a selectivity of 10. The SiO layer can also be used as a mask for etching a thin layer of SiC, since a selectivity of 1.75 between these two materials can be achieved.

**Results and discussions**

SEM images of the SiC films patterned in CF$_4$:SF$_6$:O$_2 = 70:10:10$ plasma are shown in figure 2.5. One can observe a clear anisotropic profile and a good pattern transfer in all cases.

We have studied the etch rate of a SiC layer with different deposition conditions. The etch rate was in the range from 30nm/min. to 120nm/min. as the deposition parameters vary (see appendix A.1). The ANOVA table in appendix A.2 illustrates the relative contribution of the parameters. Figure 2.6 shows the effect of deposition parameters. The change in temperature and in the SiH$_4$ gas flow rate has strong effect (> 20% contribution). The etch
2.5. Deposition and etching characteristics of PECVD SiC films

Figure 2.5: SEM images of an etched undoped SiC film (a) holes and (b) lines.

rate increases with the SiH$_4$ gas flow rate. It decreases when the deposition temperature increases.

Figure 2.6: Effect of the deposition parameters on the etch rate of SiC films.

2.5.3 Effect of doping and post deposition annealing

When attempting to expand applicability of PECVD SiC films, one needs to chemically modify them such that properties such as bandgap and resistivity change considerably. Experiments with the addition of doping during deposition as well as post-deposition annealing treatments were performed. In this section, we examine the effect of these treatments on the thickness, shrinkage, and etching characteristics of PECVD SiC films. The effect of doping as well as post-deposition annealing treatments on structural, mechanical, optical and electrical properties of PECVD SiC films will be presented in chapter 3 and 4.
Experimental

Samples with different amounts of B and P were prepared by adding borane (B$_2$H$_6$) and phosphine (PH$_3$) into the gas mixture of SiH$_4$ and CH$_4$ (in-situ doping). To study the effect of in-situ doping, we prepared two sets of samples. In the first group we varied the composition of SiC films and fixed the doping gas flow rate. In the other group, we kept the flow rate of SiH$_4$ and CH$_4$ gases constant, while changing the doping gas flow rate. The deposition parameters for in-situ doped SiC films are summarized in table 2.4.

Table 2.4: Deposition parameters for depositing in-situ doped SiC films.

<table>
<thead>
<tr>
<th>Deposition parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature (°C)</td>
<td>400</td>
</tr>
<tr>
<td>Pressure (Torr)</td>
<td>2.25</td>
</tr>
<tr>
<td>Power (W)</td>
<td>1000</td>
</tr>
<tr>
<td>CH$_4$ gas flow rate (sccm)</td>
<td>3000</td>
</tr>
<tr>
<td>SiH$_4$ gas flow rate (sccm)</td>
<td>50-250</td>
</tr>
<tr>
<td>B$_2$H$_6$, PH$_3$ gas flow rate (sccm)</td>
<td>130</td>
</tr>
</tbody>
</table>

The effect of post-deposition treatments was studied using both thermal and laser annealing. Directly after deposition, a thermal annealing cycle has been carried out in a Flexus (Tencor FLX-2908 systems), which can measure the stress of the film at the same time. Several annealed cycles from room temperature up to 400°C, 500°C and 600°C, and differing in durations have been carried out, ranging 5 minutes and 3 hours.

The laser annealing experiments were performed with an excimer laser (XMR Laser 5121 system) that uses a XeCl$_2$ UV laser ($\lambda = 308$nm) and operates with an energy of 500mJ/pulse. The repetition frequency of the laser is 30Hz. The energy density of the laser ranges from 100mJ/cm$^2$ to 160mJ/cm$^2$. The films were positioned in the chamber (without vacuum) at room temperature. The advantage of the laser annealing method is that only the SiC layer, not the underlying substrate, is exposed to the heating.

Results and discussions

Figure 2.7(a) and 2.7(b) show the deposition rate and the etch rate of in-situ doped SiC films. A clear increase in the deposition rate was observed
when adding the doping gas. The effect is more pronounced for p-type films. The etch rate is clearly affected by the doping gas level, and while for p-type films we observed a slight decrease, for n-type films a sensible increase was measured.

Figure 2.7: Effect of (a) 4% doping and different composition and (b) level doping on the deposition rate and the etch rate of SiC films.

The effect of the annealing temperature on shrinkage of undoped and in-situ doped SiC films are summarized in table 2.5. The shrinkage of SiC films is calculated as:

\[
\text{Shrinkage(\%)} = \left( \frac{t_a - t_b}{t_b} \right) \times 100\% \tag{2.1}
\]

where \(t_a\) and \(t_b\) are the thickness of the film after and before thermal annealing, respectively. Both doped and undoped SiC films shrank more after annealing. The shrinkage is more pronounced for a phosphorus doped film at 600°C. The thickness of the SiC film slightly increases in short term annealing at 400°C. This can be explained as follows. When annealing in an oxygen ambient, the amorphous SiC is oxidized and the film gradually becomes a mixture of amorphous SiC-SiO. This causes an increase in thickness as more SiO is formed. When the temperature increases, a break in bonding of Si-H and rearranging of atoms in the film occurs, causing the decrease in thickness of the SiC film.

Table 2.6 summarizes the etch rate of undoped and in-situ doped a-Si_{0.54}C_{0.46} films after the thermal annealing step at different temperatures. The etch rate decreases as the temperature increases. The etch rate of undoped SiC is lower than that of n-type SiC films, but higher than that for
Table 2.5: The shrinkage of undoped and in-situ doped a-Si$_{0.54}$C$_{0.46}$ films due to post deposition thermal annealing.

<table>
<thead>
<tr>
<th>Samples</th>
<th>400°C</th>
<th>500°C</th>
<th>600°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5min.</td>
<td>3h</td>
<td>5min.</td>
</tr>
<tr>
<td>undoped film</td>
<td>-0.6</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>p-type film</td>
<td>-0.6</td>
<td>0.0</td>
<td>0.5</td>
</tr>
<tr>
<td>n-type film</td>
<td>-0.4</td>
<td>0.8</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Table 2.6: Effect of post-deposition annealing on etch rate of undoped and in-situ doped a-Si$_{0.54}$C$_{0.46}$ films.

<table>
<thead>
<tr>
<th>Samples</th>
<th>400°C</th>
<th>500°C</th>
<th>600°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5min.</td>
<td>3h</td>
<td>5min.</td>
</tr>
<tr>
<td>undoped film</td>
<td>86</td>
<td>84</td>
<td>75</td>
</tr>
<tr>
<td>p-type film</td>
<td>90</td>
<td>80</td>
<td>74</td>
</tr>
<tr>
<td>n-type film</td>
<td>107</td>
<td>101</td>
<td>90</td>
</tr>
</tbody>
</table>

the p-type SiC film. This is because the etch rate of certain semiconductors depends on the Fermi level position [66]. In this case, we suppose that both n-type and undoped SiC films have more filled states in the bandgap and hence are chemically more reactive and have a higher etch rate than the p-type SiC film. As the doping level increases, so does the etch rate of the n-type film, while that of the p-type films decreases.

2.6 Concluding remarks

In this chapter, a brief overview of commonly used materials for the structural layer in surface micromachining has been presented. SiC films deposited by PECVD have been shown to be an excellent candidate as a structural layer for post-processing surface micromachining, since the deposition and patterning processes are carried out at low temperature (< 400°C). Furthermore, this material is inert in many chemical solutions; and thus it can easily be combined with several materials used as sacrificial layers.

The Taguchi method provides a systematic approach for depositing SiC
films by the PECVD technique. The influence of the deposition parameters on the deposition rate and the etching characteristics of the SiC films have been mapped out. Among the important parameters, the SiH₄ gas flow rate of the PECVD process plays a crucial role in controlling properties of SiC films. Furthermore, the chapter reported the strong effect of doping and annealing techniques on properties of SiC films. This investigation allows us to select the most suitable deposition condition to obtain layers with desired characteristics.
Chapter 3

Structural and mechanical properties of PECVD SiC films

3.1 Introduction

SiC films prepared by the PECVD technique are usually in an amorphous form. A close relationship between the chemical composition and properties of amorphous thin films has been observed in many investigations [40]. In section 3.2, we use electron probe X-ray microanalysis (EPMA), Fourier transfer infrared (FTIR), scanning electron microscope (SEM), atomic force microscope (AFM) and optical microscope measurements, to analyze the chemical composition and chemical bonding of SiC films prepared by the RF PECVD technique. Other structural properties of SiC films, such as roughness and pinhole density, are investigated as well. The effect of in-situ gas doping on these properties is discussed.

In order to increase the applicability of PECVD SiC films, nanocrystalline, polycrystalline, or single-crystalline SiC films are required. An interesting technique in which amorphous SiC is crystallized is laser annealing [67]. The advantage of this technique is the low-temperature processing that allows both post-processing and the use of glass substrates. In this work, we investigate the structure of laser annealed SiC films. The effect of laser energy on the electrical properties of SiC films will be discussed in chapter 4.

The mechanical behavior of thin films is important for the performance and the reliability of devices with certain functional properties, e.g., integrated circuits, magnetic discs, and magneto-electronic devices. Although the
technological fabrication of these devices has been well investigated, their performance is still restricted for various reasons. Damage by crack formation or localized plastic deformation can occur due to temperature changes, external mechanical loading, or it can even happen spontaneously during operation. The driving force in all these phenomena is the mechanical stress, which is almost unavoidable in thin films. It is therefore important to understand how this stress is related to film growth and subsequent treatment in order to control film properties and the functionality of devices realized using these films [68, 69].

In section 3.3.2, by combining the Taguchi method with least squares fitting [70], we create an empirical model for the PECVD process to control the stress of SiC films. This model allows us to investigate the effect of the deposition parameters and thus to optimize the PECVD process to obtain low tensile stress. Furthermore, we also study the effect of boron and phosphorus doping and subsequent thermal annealing on the stress of SiC films.

In section 3.3.3, we calculate the strain and Young modulus of low stress SiC films. Both are of paramount importance in the design and application of the microstructures.

3.2 Structural properties

3.2.1 As-deposited films

Chemical composition analysis

The chemical composition of PECVD SiC films was determined with EPMA. This technique uses a focused beam of high-energy electrons (5-30KeV) to non-destructively ionize a solid specimen surface (including thin films and particles) for inducing emission of characteristic X-rays (0.1-15KeV). The composition was calculated from the intensity ratio of reference and a standard sample, applying the modified approach for matrix correction [40].

Table 3.1 shows the atom percentages of the as-deposited SiC films prepared by PECVD with a temperature of 400°C, a pressure of 2.25 Torr, a power of 100W. The percentage of C atoms decreases, while that of the Si atoms increases linearly with the SiH₄ flow rate. Based on this analysis, we define a sample with a Si concentration higher than 50% as a Si-rich SiC sample. The film with a C concentration higher than 50% is indicated as a C-rich sample. These definitions will also be used in subsequent chapters.
Table 3.1: The composition of the as-deposited SiC films in weight percentage.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Gas flow rate (sccm)</th>
<th>Atom percent (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CH$_4$</td>
<td>SiH$_4$</td>
</tr>
<tr>
<td>Sample 1</td>
<td>3000</td>
<td>250</td>
</tr>
<tr>
<td>Sample 2</td>
<td>3000</td>
<td>200</td>
</tr>
<tr>
<td>Sample 3</td>
<td>3000</td>
<td>150</td>
</tr>
<tr>
<td>Sample 4</td>
<td>3000</td>
<td>100</td>
</tr>
<tr>
<td>Sample 5</td>
<td>3000</td>
<td>50</td>
</tr>
</tbody>
</table>

Chemical bonding analysis

The nature of chemical bonding between constituents of the films is studied by IR spectroscopy in an absorption mode between 400cm$^{-1}$ and 4000cm$^{-1}$. The data is analyzed by comparing the recorded spectrum to a computer simulated model with absorption features calculated from a spectroscopic database [71].

Figure 3.1(a) and 3.1(b) show the FTIR spectra of SiC thin films on Si and SiO$_2$ substrates, respectively. Four clear peaks, at 780cm$^{-1}$, 1000cm$^{-1}$, 2100cm$^{-1}$, 2860cm$^{-1}$ were detected, indicating the presence of Si-C, Si-CH$_n$, Si-H$_n$, C-H$_n$ bonds in the SiC thin films. A broad peak at 1120-1240cm$^{-1}$ for Si-O-Si bonding was observed for SiC thin films deposited on a SiO$_2$ substrate.

![Figure 3.1: FTIR spectra of SiC thin films on (a) Si and (b) SiO$_2$ substrates.](image-url)
Pinhole density

To investigate the pinhole density of PECVD SiC films, we sputtered a thin Al film under the SiC film. The sample was then immersed in an acid H₃PO₄ solution at 35°C. As this solution attacks Al but not SiC, if there are pinholes in the SiC films, the underlaying Al thin film will be damaged. Pinholes were observed in the Si-rich SiC film, while the C-rich film did not have any pinhole. The pinhole density was approximately 4-5 holes/cm². Figure 3.2 shows the SEM image of one pinhole of a Si-rich SiC film after being immersed into the acid solution for two hours.

![SEM image of pinhole](image)

Figure 3.2: SEM image of the pinhole of a Si-rich SiC film after being immersed into the acid solution.

3.2.2 The effect of in-situ doping

Chemical composition analysis

The chemical compositions of the in-situ doped SiC films are given in table 3.2. The composition of the SiC varies somewhat between the specimens. The accuracy of the measurement is 0.3% for B, 0.6% for C, 1.0% for Si and 0.2% for P. From these evaluations it can be assumed that when P atoms are added, they replace C positions in the bonding between C and Si while B atoms replace Si positions.

Chemical bonding analysis

Figures 3.3(a) and 3.3(b) show the FTIR spectra of in-situ n-type and p-type SiC films, respectively. Like undoped SiC thin films, all samples show clear peaks indicating the presence of Si-C, Si-CH₃, Si-H₃, C-H₃ bonds. In addition,
Table 3.2: The composition of the doped samples in weight percentage.

<table>
<thead>
<tr>
<th>Samples</th>
<th>CH₄</th>
<th>SiH₄</th>
<th>PH₃</th>
<th>B₂H₆</th>
<th>C</th>
<th>Si</th>
<th>P</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>un-SiC film</td>
<td>3000</td>
<td>250</td>
<td>0.0</td>
<td>0.0</td>
<td>31.0</td>
<td>69.0</td>
<td>0.0</td>
<td>0.0</td>
</tr>
<tr>
<td>2P-SiC film</td>
<td>3000</td>
<td>250</td>
<td>70</td>
<td>0.0</td>
<td>27.4</td>
<td>70.2</td>
<td>2.4</td>
<td>0.0</td>
</tr>
<tr>
<td>4P-SiC film</td>
<td>3000</td>
<td>250</td>
<td>140</td>
<td>0.0</td>
<td>25.1</td>
<td>70.4</td>
<td>4.5</td>
<td>0.0</td>
</tr>
<tr>
<td>8P-SiC film</td>
<td>3000</td>
<td>250</td>
<td>280</td>
<td>0.0</td>
<td>23.4</td>
<td>68.0</td>
<td>8.6</td>
<td>0.0</td>
</tr>
<tr>
<td>2B-SiC film</td>
<td>3000</td>
<td>250</td>
<td>0.0</td>
<td>70</td>
<td>30.7</td>
<td>69.3</td>
<td>0.0</td>
<td>*</td>
</tr>
<tr>
<td>4B-SiC film</td>
<td>3000</td>
<td>250</td>
<td>0.0</td>
<td>140</td>
<td>30.2</td>
<td>61.4</td>
<td>0.0</td>
<td>8.4</td>
</tr>
<tr>
<td>8B-SiC film</td>
<td>3000</td>
<td>250</td>
<td>0.0</td>
<td>280</td>
<td>28.9</td>
<td>56.5</td>
<td>0.0</td>
<td>14.6</td>
</tr>
</tbody>
</table>

* The result could not be analyzed due to the resolution limit of B detection (0.1%)

Figure 3.3: FTIR spectra of in-situ doped SiC thin films (a) n-type, and (b) p-type.

A peak at 1150 cm⁻¹ detects tetra trigonally coordinated B (B(OH)₃) in the p-type film. The effect of the dopant on Si-C bonds is visible.

In case of n-type SiC thin films, the Si-C peak shifts to the lower wavenumber compared to the Si-C bond in undoped SiC thin films (780 cm⁻¹ → 775 cm⁻¹), which implies that the Si-C bond is slightly stronger. Weaker Si-C bonding is observed for p-type film since the peak shifts to the higher wavenumber (780 cm⁻¹ → 782 cm⁻¹). The model in figure 3.4 explains the
change in bonding of Si-C in a SiC molecule. It can be explained by the fact that the Si-C bond in a SiC molecule is slightly polar due to the difference in electronegativities between two atoms, \( (\chi_C = 2.55, \chi_{Si} = 1.9) \); the C atom is slightly negative \( (\delta_0^-) \) and the Si atom slightly positive \( (\delta_0^+) \). As the P atom replaces the C position in a SiC molecule in the bond between P and Si atoms, its spare electron tends to go into the Si atom, so that the polarization between Si-C bonding is reduced \( (\delta_2 < \delta_0) \); the bond becomes stronger \( (c < a) \). When a B atom is added into a SiC molecule replacing the Si atom, it will pull the electron from the C atom to itself. As the polarization between C-Si is stronger \( (\delta_1 > \delta_0) \) thus \( (a < b) \), the bonding between C and Si atoms gets weaker.

### 3.2.3 The effect of laser annealing

A post-annealing step by laser is used to obtain crystalline structures in SiC films. In this section we examine the effect of XeCl₂ excimer laser annealing on the structural properties of undoped and in-situ doped PECVD SiC thin films. A variety of laser intensities and pulsed densities have been used. The experimental conditions are described in section 2.5.3.

Table 3.3 indicates the roughness value of these films with a variety of laser intensity and pulsed densities. The annealed conditions are pos.1: non-annealed, pos.2: 160mJ/cm² with six shots, pos.3: 160mJ/cm² with ten shots, pos.4: 140mJ/cm² with six shots, and pos.5: 140mJ/cm² with ten shots. The obtained results show that the roughness increases with both the laser intensity and the pulse density.

Figures 3.5(a-d) illustrate the topographies of undoped and in-situ doped
Table 3.3: Roughness of undoped and in-situ doped a-Si$_{0.54}$C$_{0.46}$ surfaces with different laser annealing energies.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Roughness (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pos.1</td>
</tr>
<tr>
<td>undoped film</td>
<td>58</td>
</tr>
<tr>
<td>p-type film</td>
<td>31</td>
</tr>
<tr>
<td>n-type film</td>
<td>69</td>
</tr>
</tbody>
</table>

Figure 3.5: AFM topographies of undoped SiC thin films (a) prior to and (b) after laser annealing with 160mJ/cm$^2$, and AFM topographies of (c) p-type and (b) n-type SiC thin films after laser annealing with 160mJ/cm$^2$.

SiC films prior to and after laser annealing. AFM images of the film surfaces reveal that the surface roughness of laser annealed films increases compared to that of as-deposited films.
From the AFM analysis, we have observed the cubic structures on the surface laser annealed films. This indicates the existence of nano-polycrystalline structures [67]. The grain size is quite uniform, approximately 100nm. The structure of the p-type SiC thin film was modified most by the laser annealing as indicated by the numerous crystallites observed. It can be concluded that laser annealed SiC thin films have been changed into nano-polycrystalline forms through an effective process of structure re-ordering.

3.3 Mechanical properties

In this section, we present three most relevant mechanical properties of PECVD SiC films, namely stress, strain and Young modulus.

3.3.1 Mechanical measurements

Stress

Stress is the internal resistance of a material to the distorting effects of an external force or load. The various types of stresses can generally be classified into one of the following six categories

- Residual stress, which is due to the manufacturing process that leaves stress in the material.
- Structural stress, which is produced in structural membranes because of the weights they support.
- Pressure stress, which is induced in vessels containing pressurized materials.
- Flow stress, which occurs when a mass of flowing fluid induces a dynamic pressure on a conduit wall.
- Thermal stress, which exists whenever temperature gradients are present in the material.
- Fatigue stress, which is due to cyclic application of a stress.

The stress $\sigma$ can be calculated as follows:

$$\sigma = \frac{F}{A} \quad (3.1)$$

where $A$ is the area on which the force $F$ is applied.
Many stress measurement techniques have been reported. They include the wafer curvature technique [72], the beam buckling technique [73], and resonant frequency analysis [74]. The main tool for thin-film stress measurement is the wafer curvature technique, which gives information about (i) stress development during film deposition, and (ii) stress changes during thermal treatment.

![Diagram of wafer curvature](a) and (b) tensile stress.

Figure 3.6: The curvature of a wafer due to (a) compressive stress and (b) tensile stress.

When a layer is deposited on top of a substrate, the stress in the thin film causes the whole wafer to curve up or down, depending on the stress (see figure 3.6). If the film is compressive, it causes a convex surface. Otherwise, the surface is concave. By measuring the curvature prior to and after deposition of the thin film, one can calculate the stress \( \sigma \) using the Stoney formula [66]

\[
\sigma = \frac{Eh^2}{(1-\nu)6Rt}
\]

where \( \frac{E}{(1-\nu)} \) is the biaxial elastic modulus of the substrate (MPa/m), \( h \) is the substrate thickness (m), and \( t \) is the film thickness (m). The radius \( R \) of the curvature of the substrate can be calculated as

\[
R = \frac{R_1R_2}{R_2 - R_1},
\]

where \( R_1 \) and \( R_2 \) are the radius of the curvature prior to and after deposition of the film.

The advantage of this method is that one need have no knowledge of material properties to determine volume averaged stresses in a thin film. On the other hand, the disadvantage is that it only works on an unpatterned sheet of film and not on the structured layer [72].

**Strain**

A given state of stress usually exists in a considered volume of a material. Reaction of the atomic structure will manifest itself on a macroscopic scale.
Therefore, whenever a stress is applied to a material, a proportional dimensional change or distortion takes place. Such a proportional dimensional change (the intensity or degree of the distortion) is called strain. It measures the total elongation per unit length of the material due to the applied stress. The following equation illustrates this proportion $\epsilon$

$$\epsilon = \frac{\delta}{L}$$  \hspace{1cm} (3.4)

where $\delta$ is the total elongation and $L$ is the original length.

There are two forms of strain:

- Elastic strain (or elastic deformation), which is a transitory dimensional change that exists only while the initiating stress is applied and disappears immediately upon its removal.

- Plastic strain (or plastic deformation), which is a dimensional change that remains after the initiating stress is removed.

A direct way to observe and measure strain in a thin film is to fabricate test structures. Once these structures have been partly released from the substrate, buckling or other changes in shape can be observed with an optical microscope.

An accurate and simple method to measure the strain is to use a rotating beam structure (see figure 3.7). With this structure, the expansion due to strain is converted into a rotation. The rotation acts as an amplification of the expansion, providing a measurable displacement of the tip, which is proportional to the strain.

When the stress of the film is compressive (or tensile), beams A and B shrink (or extend) and they push (or pull) the central beam C. The beam C will rotate counterclockwise for compressive stress and clockwise for tensile stress.

The strain $\epsilon$ can be calculated as a function of the displacement of the tip $y$ with the following formula

$$\epsilon = y \times \frac{O}{(L_A + L_B) \times (L_C + \frac{1}{2}O)}$$  \hspace{1cm} (3.5)

where $L_A$, $L_B$, $L_C$ and $O$ are distances shown in figure 3.7.
Figure 3.7: Geometry of a rotating beam structure.

Young’s modulus

Young’s modulus (sometimes referred to as modulus of elasticity, meaning the “measure” of elasticity) is an extremely important characteristic of a material. It is the numerical evaluation of Hooke’s law, namely the ratio of stress to strain (the measure of resistance to elastic deformation). To calculate the Young’s modulus $E$, one must divide the stress at any point below the proportional limit by the corresponding strain

$$E = \frac{\sigma}{\epsilon}, \tag{3.6}$$

where $\sigma$ is the stress and $\epsilon$ is the strain.

3.3.2 Process optimization for low tensile stress films

Control of the stress in the structural layer is important in the processing of surface micromachined structures. Compressive stress may cause undesired buckling and bending of the released micromachined structures. In addition, cracking may occur if the tensile stress is too high. Here we first employ the Taguchi method to investigate the influence of deposition parameters on the stress. A mathematical model is introduced to determine an optimal setting.

Effect of deposition parameters on stress

The preparation conditions of SiC films are discussed in section 2.5.1. The stress of SiC films was measured by the curvature technique. The actual
ANOVA calculation for data analysis is shown in appendix A.5.

Figure 3.8 presents the stress response with respect to the individual variables. Figures 3.9(a-j) illustrate the 3D surface plots of the stress as a function of deposition parameters.

Figure 3.8: Effect of deposition parameters on the stress of 500nm SiC films.
Figure 3.9: Effect of interaction between deposition parameters on the stress of SiC films: (a) T - P, (b) G - T, (c) T - HF, (d) T - LF, (e) P - G, (f) P - HF, (g) P - LF, (h) G - HF, (i) G - LF, (j) LF - HF.
of the deposition parameters. The results show that the pressure and the SiH$_4$ gas flow rate are the most influential factors. The results also indicate that the temperature and LF component can affect the stress of SiC films significantly, while the HF component is not as relevant.

Mathematical modelling

After having found out which parameters are important for a process, we have to determine their optimal settings. The use of a mathematical model to describe the effects of deposition parameters allows us to represent the parameter influences in a simple way and to predict the results of experiments with different parameter combinations. Polynomial models can give an adequate description of variable relationships; of these, quadratic models are most commonly used.

Let $y$ denote the output of the experiment and $x_i, 1 \leq i \leq N$ the $N$ influence factors that we wish to model. The general form of a full quadratic model, which includes linear and two-factor interactions, is as follows [75]

$$y = b_0 + \sum_{i=1}^{N} b_i x_i + \sum_{i=1}^{N} \sum_{j=i+1}^{N} b_{ij} x_i x_j + \sum_{i=1}^{N} b_{ii} x_i^2$$  \hspace{1cm} (3.7)

where $b_i$, $b_{ij}$ and $b_{ii}$ are the model parameters. By substituting the values of $y$ and the $x_i$s obtained from the experiments into eq. (3.7), we obtain a system of linear equations with unknown $b_i$, $b_{ij}$ and $b_{ii}$. This system of linear equations can be solved by the standard least-squares method.

For the purpose of this chapter, $y$ is the stress, and the $x_i$s, $i=1...5$ the process parameters, namely the temperature, the pressure, the SiH$_4$ gas flow rate, the HF and LF components. Specifically, $x_i$ are normalized as below

$$x_i = 2 \times \frac{factor - x_i^{mean}}{x_i^{max} - x_i^{min}}$$  \hspace{1cm} (3.8)

where $x_i^{max}$ and $x_i^{min}$ are the maximum and minimum value in the selected range respectively, and $x_i^{mean}$ is their average value

$$x_i^{mean} = \frac{x_i^{max} + x_i^{min}}{2}$$  \hspace{1cm} (3.9)

This model considers five process parameters and has 21 coefficients in total. The result of the least-squares calculation is
\[
\begin{align*}
y &= -403 - 119.89 \times x_1 + 136.5 \times x_2 + 159.8 \times x_3 - 11.3 \times x_4 \\
& \quad - 98 \times x_5 - 55.5 \times x_1x_5 - 26.8 \times x_2x_3 - 57.5 \times x_2x_4 \\
& \quad + 11.7 \times x_2x_5 + 4.6 \times x_3x_4 + 3.8 \times x_3x_5 \\
& \quad - 19 \times x_4x_5 + 49 \times x_2^2 + 43.65 \times x_5^2
\end{align*}
\] (3.10)

The model indicates that the SiH\(_4\) gas flow rate (\(x_3\)) and the pressure (\(x_2\)) are the most influential parameters. This equation is in good agreement with the ANOVA calculation. It is also interesting to observe that if some parameters do not interact with each other, their combination coefficients are zero.

**Confirmation experiments**

The stress of a PECVD SiC film can be adjusted by varying the deposition parameters, according to the demand of a specific application. Our goal is to optimize the deposition parameters to get low tensile stress SiC films.

According to the results shown in figure 3.8, the optimal parameter values could be obtained without considering interaction between factors. The winner for each parameter is a temperature of 300°C, a pressure of 2.5 Torr, a SiH\(_4\) gas flow rate of 250 sccm, an HF component of 500 W, and a LF component of 250 W. The stress of the SiC film in this case is 97.5 MPa.

Considering the interaction between factors, eq. (3.10) suggests alternative values for the deposition parameters to obtain a low tensile stress SiC film. Table 3.4 shows the measured and calculated values of the stress to validate the model. Note that by considering the interaction between factors, we have reduced the stress down to 22.5 MPa.

**Table 3.4: Recipes for 500nm low tensile stress SiC films.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>(T) (°C)</th>
<th>(P) (Torr)</th>
<th>(\text{SiH}_4) gas (sccm)</th>
<th>(\text{HF}) (W)</th>
<th>(\text{LF}) (W)</th>
<th>(\sigma_{\text{cal.}}) (MPa)</th>
<th>(\sigma_{\text{meas.}}) (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>300</td>
<td>2.5</td>
<td>250</td>
<td>500</td>
<td>250</td>
<td>+ 106.04</td>
<td>+ 97.5</td>
</tr>
<tr>
<td>2</td>
<td>400</td>
<td>2.5</td>
<td>250</td>
<td>500</td>
<td>250</td>
<td>+ 30.86</td>
<td>+ 34.0</td>
</tr>
<tr>
<td>3</td>
<td>400</td>
<td>1.8</td>
<td>250</td>
<td>250</td>
<td>450</td>
<td>+ 10.20</td>
<td>+ 22.5</td>
</tr>
</tbody>
</table>
In conclusion, the stress of PECVD SiC films can be controlled via the deposition parameters to obtain the low tensile stress. The agreement between the experimental and theoretical results has proved that this is a proper method for experimental design. These low tensile stress PECVD SiC films will be used for applications in chapter 6.

The effect of in-situ doping

The preparation condition of in-situ doped SiC films can be seen in section 2.5.3. Figure 3.10(a) shows the effect of in-situ doping on stress of a SiC film. The stress of in-situ doped SiC films tends to the tensile region and is somewhat larger than that for undoped films. We observed stronger changes in stress toward the tensile direction for p-type film than for n-type film. The changing in stress depends on the doping gas level of a SiC film can be seen in figure 3.10(b). For the n-type films, the increase in stress is very small and almost insensitive to the doping gas level, while for the p-type films, the effect of doping level is much more pronounced.

![Figure 3.10: Effect of (a) 4% doping and different composition and (b) doping gas level on the stress of SiC films.](image)

A small effect on stress was observed for a low nominal doping level (< 2%) and a very strong one at a higher doping level. This is because the structure of the layer changes when dopants are added. As reported earlier [66] the stress of a SiC film is affected by the Si/C ratio. In fact, a shift from the compressive toward the tensile region is obtained by increasing the SiH₄/CH₄ gas ratio. This effect explains why larger stress was observed for the p-type SiC film compared to the n-type SiC film at the same doping level.
The effect of thermal annealing

A post deposition thermal annealing was carried out in air. The temperature was raised with a speed of 10°C/min, kept at 400°C, 500°C and 600°C for three hours, and then cooled down to room temperature. The typical effect of annealing on stress of a SiC film up to 500°C is shown in figure 3.11.

![Diagram](https://via.placeholder.com/150)

Figure 3.11: Effect of temperature and annealing time on stress of a SiC film.

The stress-time curve shows a change during a heating/cooling cycle. The diagram can be divided into three sections: (i) the temperature increases to 500°C, (ii) constant temperature at 500°C, and (iii) cooling down. In the first section of the diagram, the stress increases to maximum in compression (minimum in diagram). This is due to different thermal expansion coefficients of Si and SiC. At the temperature 500°C, the chemical composition and structure of the layer change, and the time-dependent stress is an exponential function. Wuu et al. [76] observed a decrease in Si-H bonds in a-SiC films after heat treatment. They suppose that the stress behavior of the a-SiC films is related to Si-H bond breaking, changing the stress toward tensile. In the cooling part, the diagram is dominated by the different thermal expansion coefficients of Si and SiC, like in the first period but in a reverse manner. Cooling down reduces the stress approximately as much as heating increased it.

Figure 3.12 shows the film stress as a function of the annealing temperature for 500nm SiC films prepared at different deposition temperatures. The expansion coefficients of the SiC films increase with the deposition temperature. The strongest change in stress was observed for the SiC film prepared at 300°C.

The corresponding stress levels prior to and after 5 minutes and 3 hours thermal cycles of the SiC films are plotted in figure 3.13.
Figure 3.12: The effect of thermal annealing on the stress of SiC films prepared at three deposition temperatures.

Figure 3.13: The effect of thermal annealing on stress of undoped and in-situ doped SiC films after 5 minutes and 3 hours thermal annealing.

Annealing at 500°C and 600°C for three hours drastically changes the film stress, which becomes high tensile stress, independent of the deposition parameters. After annealing, we observed a uniform change in color of the layers and no cracking of the films.

3.3.3 Strain and Young’s modulus

Five rotating beam structures of a 1µm SiC film with different rotation point widths (1µm, 1.5µm, 2µm, 2.5µm and 3µm) have been prepared to measure the strain of a SiC film. The width of the rotating points was varied to show the influence of the stiffness on the deflection. The length and width of these
3.4 Concluding remarks

Figure 3.14: Rotating beam structures of a SiC film with rotation point widths of 1.5\(\mu\)m, 2\(\mu\)m and 3\(\mu\)m.

beams are \(L_A = L_B = L_C = 50\mu\)m, \(W_A = W_B = W_C = 5\mu\)m. The process to prepare these structures can be seen in appendix B.5. Figure 3.14 shows a SEM image of three rotating beams with a width of 1.5\(\mu\)m, 2\(\mu\)m and 2.5\(\mu\)m. A slight clockwise rotation for the low tensile stress SiC film was observed. In this case, the strain and the Young modulus were \(1.09 \times 10^{-4}\) and 460 GPa, respectively.

3.4 Concluding remarks

This chapter presented the structural and mechanical properties of SiC films prepared by the PECVD technique. The effects of deposition parameters, doping and post-deposition annealing on the properties have been investigated.

The obtained results show that the chemical composition affects the properties of a-SiC films. Structure re-ordering in PECVD SiC films from an amorphous to a nano-polycrystalline state has been observed after post-deposition laser annealing.

By combining an experimental design method with a mathematical technique, we have obtained an empirical model to control the PECVD process. This empirical model takes into account the interaction between factors, which allows us to select the proper parameter values to prepare a low tensile stress SiC film as required for surface micromachined devices. Furthermore, the control on stress in SiC films has been outlined by showing the influence of doping and post deposition thermal annealing.
Chapter 4

Optical and electrical properties of PECVD SiC films

4.1 Introduction

The electrical and optical properties of c-SiC depend strongly on its specific crystal structures. For a-SiC films, the optical and electronic properties can be tailored by changing the bonding configuration through specific selection of the deposition parameters. Moreover, fundamental changes in the electro-optical characteristics of a-SiC films occur with in-situ doping and post-deposition annealing [77, 78, 79]. This chapter describes the optical and electrical properties of a-SiC films prepared by the PECVD technique and the effect of doping and post deposition annealing on these properties.

In section 4.2, we investigate the optical properties of a-SiC films. A brief review is given on the spectroscopy ellipsometry technique and theoretical models, including the Tauc model, the Wemple and DiDominico model and the Spitzer and Fan model. Important optical constants of the film, such as the bandgap, the refractive index, the dielectric constant, the dispersion energy and the oscillator energy, are calculated. The influence of the deposition parameters, and of doping and post-deposition thermal annealing on the optical constants of the a-SiC films are also presented.

As for the electrical properties, in section 4.3, we report measurements of the sheet resistance of a-SiC films with different doping gases and compositions using van der Pauw structures. The effect of laser annealing on electrical properties of a-SiC is also investigated. By measuring the I-V and C-V char-
acteristics of metal-insulator-metal (MIM) and metal-insulator-semiconductor (MIS) structures, the conduction mechanism in the a-SiC films is proposed. Electrical constants such as the dielectric constant, the breakdown voltage, the leakage current density, and the flat band voltage for both doped and undoped thin films are calculated as well.

4.2 Optical properties

Information about spectral dependence of optical parameters such as the dielectric constant, the refractive index, the reflectivity and the absorption coefficient are essential in the characterization of materials used in the fabrication of opto-electronic devices.

4.2.1 Spectroscopic ellipsometry of thin films

One of the effective techniques to characterize the optical properties of thin films is spectroscopic ellipsometry [80, 81]. This technique measures the change in the polarization state of light reflected from the sample’s surface. Figure 4.1 shows the reflections and transmissions with multiple interfaces. $N_1$, $N_2$ and $N_3$ are the complex indices of the refraction of air, film, and bulk, respectively. $\Phi_1$ is the angle of incidence, while $\Phi_2$ and $\Phi_3$ are angles of refraction in film and bulk, respectively. The thickness of the film is denoted by $d$.

The fundamental equation of spectroscopic ellipsometry is:

$$\tan \psi e^{i\Delta} = \frac{R_P}{R_S}$$

(4.1)

Figure 4.1: Reflections and transmissions with multiple interfaces.
where $R^p$ is the reflection coefficient in the plane of incidence and $R^s$ the reflection coefficient in the plane wave polarized perpendicular to the plane of incidence. $\Delta$ is the change in phase difference that occurs upon reflection, and $\psi$ is the angle whose tangent is the ratio of the magnitude of the total reflection coefficient. Both $\Delta$ and $\psi$ are the quantities measured by an ellipsometer.

The coefficients $R^p$ and $R^s$ are calculated as follows:

\[
R^p = \frac{r^p_{af} + r^p_{fb} \exp(-i2\beta)}{1 + r^p_{af} r^p_{fb} \exp(-i2\beta)} \tag{4.2}
\]

\[
R^s = \frac{r^s_{af} + r^s_{fb} \exp(-i2\beta)}{1 + r^s_{af} r^s_{fb} \exp(-i2\beta)} \tag{4.3}
\]

where the Fresnel reflection coefficients $r_{af}$ and $r_{fb}$ are the ratios of the amplitude of the reflected wave to that of the incident wave for air-film and film-bulk interfaces, respectively,

\[
r_{af} = \frac{N_2 \cos \Phi_1 - N_1 \cos \Phi_2}{N_2 \cos \Phi_1 + N_1 \cos \Phi_2} \tag{4.4}
\]

\[
r_{fb} = \frac{N_3 \cos \Phi_2 - N_2 \cos \Phi_3}{N_3 \cos \Phi_2 + N_2 \cos \Phi_3} \tag{4.5}
\]

and $\beta$ is the film phase thickness given by

\[
\beta = 2\pi \left( \frac{d}{\lambda} \right) N_2 \cos \Phi_2, \tag{4.6}
\]

The complex index of refraction, $N$, described as the interaction of light with the material is a combination of a real part and an imaginary part

\[
N = n - ik, \tag{4.7}
\]

where $n$ is the refraction index and $k$ the extinction coefficient.

The optical absorption coefficient $\alpha$, the transmission $T$, and the reflectivity $R$ can be calculated through the following relations:
\[ \alpha = \frac{4\pi k}{\lambda} \]  
(4.8)

\[ R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \]  
(4.9)

\[ T = \frac{(1 - R)^2 \exp(-\alpha d)}{1 - R^2 \exp(-2\alpha d)} \]  
(4.10)

where \( d \) is the film thickness and \( \lambda \) the wavelength of the incident light. In general, these optical properties are correlated to the electronic properties of the material.

### 4.2.2 Theoretical models for determining optical parameters

Spectroscopic ellipsometry is a powerful technique to characterize thin films. However, the data obtained from a spectroscopic ellipsometry measurement is not useful by itself. If one is interested in the film thickness, the surface roughness, the optical functions of bulk or thin film materials, one must first model the near-surface region of the sample to obtain the complex reflection coefficients \[82].

#### The Tauc model

Electronic transitions between the valence and conduction bands in the crystal start at the absorption edge, which corresponds to the minimum energy difference \( E_g \) between the lowest minimum of the conduction band and the highest maximum of the valence band. When the semiconductor becomes amorphous, one observes a shift of the absorption edge either towards lower or higher energies. In many amorphous compound semiconductors, the absorption edge has the shape shown in figure 4.2.

In high absorption regions, one can determine the optical bandgap \( E_g \) according to the following equation \[83]:

\[ \alpha E_{ph} = B(E_{ph} - E_g)^2, \]  
(4.11)

where \( E_{ph} = \hbar \nu \) is the energy of the incoming photons and \( B \) is a constant proportional to the square of the density of states. The intercept of the Tauc slope with the photon energy axis gives the optical bandgap.

The value \( E_{04} \) is defined as the absorption energy at \( \alpha = 10^4 \text{cm}^{-1} \). This energy value belongs to the exponential region of the absorption edge and
4.2. Optical properties

![Graph showing absorption edge]

Figure 4.2: The shape of the absorption edge of general amorphous compound semiconductors. There are three parts: a high absorption region A ($\alpha > 10^4 \text{cm}^{-1}$), an exponential part B which extends over four orders of magnitude of $\alpha$, and a weak absorption tail C.

is almost temperature independent at low temperature (usually below room temperature).

The Wemple and DiDomenico model

Polarizability of solids is proportional to the real part of the dielectric constant $\epsilon_1 = n^2 - k^2$. In the region where the material is transparent, the refraction index $n$ is equal to $\sqrt{\epsilon_1}$ and related to the absorption of the material by the Kramers-Kronig dispersion relation:

$$\epsilon_1(0) = 1 + \frac{2}{\pi} \int_0^\infty \frac{\nu \epsilon_2(\nu)}{\nu^2 - \omega^2} d\nu$$  \hspace{1cm} (4.12)

which was deduced under very general conditions and is valid for amorphous materials, liquids as well as for crystals. Here, $\omega$ is the frequency, while $\nu = \frac{1}{\omega}$.

If there is negligible absorption due to lattice vibrations, impurities or defects, the refraction index at zero frequency $n_0$, corresponding to the electronic transitions, is identical to the refractive index measured at low frequency defined from the relation:

$$n_0^2 = \epsilon_1(0)$$

$$= 1 + \frac{2}{\pi} \int_0^\infty \omega \epsilon_2(\omega) d\omega$$ \hspace{1cm} (4.13)
where $\epsilon_2(\omega)$ is the imaginary part of the dielectric constant and related to electronic transitions.

The dispersion data of the refractive index can be described by a single effective oscillator:

$$n^2(\omega) = 1 + \frac{E_o E_d}{E_o^2 - (h'\omega)^2}$$  \hspace{1cm} (4.14)

where $h' = h/2\pi$ with $h$ being Plank’s constant, $\omega$ the frequency, $h'\omega$ the photon energy, $E_o$ the oscillator energy (eV), and $E_d$ the dispersion energy (eV). This equation is applicable for amorphous materials, describing the frequency dependence of the refraction index of semiconductors and insulators close to zero frequency ($\omega = 0$) with two adjustable parameters $E_o$ and $E_d$. From this equation, the values of $E_o$ and $E_d$ can be obtained by plotting $\frac{1}{n^2-1}$ versus $\omega^2$ [84].

**The Spitzer and Fan model**

We first write a general relation that connect an integral of $\epsilon_2(\omega)$ over the fundamental absorption band with the concentration of the electron $N$ is

$$\int \omega \epsilon_2(\omega)d\omega = 2e^2 \pi^2 \frac{N}{m^*},$$  \hspace{1cm} (4.15)

where $m^*$ is the effective mass (kg) which is calculated as

$$m^* = \frac{m_v m_c}{m_v + m_c}$$  \hspace{1cm} (4.16)

and $N$ is the ratio of the carrier concentration to the effective mass ratio. This value is related to the thermal equilibrium concentration and to the Fermi energy level [85].

The contribution of the $\frac{N}{m^*}$ to the real dielectric constant is expressed as:

$$\epsilon_r = n^2 - k^2$$

$$= \epsilon_\infty - \frac{e^2}{\pi c^2 m^*} \lambda^2$$  \hspace{1cm} (4.17) \hspace{1cm} (4.18)

where $\epsilon_\infty$ is the high-frequency dielectric constant, $e$ is the electronic charge (C), and $c$ is the velocity of light (m/s).
The values of $\frac{N}{m_\pi}$ and $\epsilon_\infty$ are estimated by fitting $\epsilon_r$ versus $\lambda^2$ with a straight line. From the equation 4.13, the electric free carrier susceptibility is determined [86].

### 4.2.3 Experimental

The preparation conditions of undoped and in-situ doped a-SiC films are described in section 2.5.1 and 2.5.3, respectively. All optical measurements were carried out on a spectroscopic ellipsometer (SOPRA-ES4T) at room temperature. The behaviors of tan $\psi$ and cos $\Delta$ as a function of wavelength in the range from 250nm to 800nm were measured. Based on these values, we have used computer added simulations to predict the refractive index $n$, the extinction coefficient $k$, and the optical constants $\epsilon_1$ and $\epsilon_2$.

### 4.2.4 Results and discussions

#### The absorption coefficient

Figures 4.3(a) and 4.3(b) show the absorption coefficients of undoped a-SiC films with different chemical compositions and in-situ doped in both n- and p-type films as a function of energy, respectively. The absorption increases throughout the whole band tail region with the increasing Si/C atom ratio. The curves of the absorption coefficient of both undoped and in-situ doped Si-rich a-SiC films are similar to the one desired for many amorphous compound semiconductors (see figure 4.2). In the samples of undoped and in-situ doped C-rich films, it is difficult to define three absorption regions since the curves are broadened.

The effect of the dopant concentration on the absorption coefficient of Si-rich films was investigated. Figures 4.4(a) and 4.4(b) show the absorption coefficient for both in-situ doped a-SiC films in the low-energy region (< 2.5eV). The sub-gap absorption tail (the Urbach tail) rises with increasing dopant concentration. The absorption coefficient of p-type films changed significantly more than that of n-type films. As the Urbach tail is related to the disorder in the material structure [87], we suppose that with a higher doping concentration, in-situ doped a-SiC films become less dense due to the higher deposition rate of these films. This effect is more pronounced for p-type than for n-type films.
Figure 4.3: The absorption coefficient of (a) undoped a-SiC films with different compositions and (b) in-situ doped for both C-rich and Si-rich a-SiC films.

Figure 4.4: The absorption coefficients of (a) n-type and (b) p-type a-SiC films prepared with different doping gas levels.

**Transmission and reflection**

The transmission $T$ and reflection $R$ of the undoped a-SiC films are shown in figure 4.5(a) and 4.5(b), respectively. The influence of chemical compositions on these properties can clearly be observed. The shift of the transmission edge to lower photon energy with an increase in the Si/C ratio demonstrates a similar absorption edge shift, which in turn indicates a change in the energy
spectrum of the electronic states. The maxima appearing in the reflection spectrum of a-SiC film shifts to a higher wavelength as the Si/C ratio increases. The sum \((R + T)\) gets very low because in the spectral range considered, most photons are absorbed by the sample.

Figures 4.6(a) and 4.6(b) show the effect of the doping gas level on the transmission and reflection of p-type and n-type a-SiC films, respectively. A strong shift to a lower photon energy is observed with an increase in the dopant concentration. This effect is more pronounced in p-type than in n-type films.

The optical absorption edge of the film increases with the annealing tem-
Figure 4.7: The influence of post-deposition thermal annealing on transmission and reflection of (a) undoped, (b) n-type, and (c) p-type a-SiC films.

Per temperature. Typically, this blue shift can be interpreted as either of the following:

- The formation of nanoclusters of a-SiC surrounded by SiO and quantum confinement causes the blue shift.

- The homogeneous alloying of a-SiC and SiO. In the amorphous state, the bonding of Si-C and Si-O can be quite similar.

Figures 4.7(a), 4.7(b) and 4.7(c) show that the band edge toward a low wavelength of undoped, n-type and p-type a-SiC films slightly shifts toward a low wavelength as both the temperature and the time increase. We found no change in transmission and reflection of the samples annealed in a vacuum environment.
Calculated optical constants

Bandgap
Figure 4.8(a) and 4.8(b) show the influence of the various deposition parameters on the Tauc gap ($E_g$) and the absorption gap at $\alpha = 10^4 \text{cm}^{-1} (E_{04})$ of the a-SiC films, respectively. The $E_g$ and $E_{04}$ are in the range from 2eV to 3eV. The SiH$_4$ gas flow rate has a strongest influence in the $E_g$ and $E_{04}$. Both values decrease as SiH$_4$ gas flow rates decrease. The temperature and the pressure have strong effect on $E_g$, but not on $E_{04}$. The HF and LF components have almost no effect on the $E_g$ and $E_{04}$ of the films. The contribution of all deposition parameters on the optical constants of the a-SiC films can be seen in table 4.3.

A decrease in the optical bandgap is observed for the p-type a-SiC films

Figure 4.8: The effect of deposition parameters on (a) $E_g$ and (b) $E_{04}$ of a-SiC films.
Table 4.1: Influence of post-deposition annealing on bandgap of undoped and in-situ doped $\text{a-Si}_{0.54}\text{C}_{0.46}$ films.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Bandgap $E_g$ (eV)</th>
<th>Non anneal</th>
<th>400°C</th>
<th>500°C</th>
<th>600°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>5 min.</td>
<td>3h.</td>
<td>5 min.</td>
<td>3h.</td>
</tr>
<tr>
<td>undoped film</td>
<td>2.5</td>
<td>2.6</td>
<td>2.7</td>
<td>2.8</td>
<td>2.9</td>
</tr>
<tr>
<td>n-type film</td>
<td>2.6</td>
<td>2.6</td>
<td>2.65</td>
<td>2.65</td>
<td>2.7</td>
</tr>
<tr>
<td>p-type film</td>
<td>2.5</td>
<td>2.5</td>
<td>2.6</td>
<td>2.65</td>
<td>2.7</td>
</tr>
</tbody>
</table>

Table 4.2: Influence of post-deposition annealing on absorption energy of undoped and in-situ doped $\text{a-Si}_{0.54}\text{C}_{0.46}$ films.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Absorption energy $E_{04}$ (eV)</th>
<th>Non anneal</th>
<th>400°C</th>
<th>500°C</th>
<th>600°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>5 min.</td>
<td>3h.</td>
<td>5 min.</td>
<td>3h.</td>
</tr>
<tr>
<td>undoped film</td>
<td>2.55</td>
<td>2.56</td>
<td>2.6</td>
<td>2.62</td>
<td>2.76</td>
</tr>
<tr>
<td>n-type film</td>
<td>2.36</td>
<td>2.37</td>
<td>2.4</td>
<td>2.43</td>
<td>2.45</td>
</tr>
<tr>
<td>p-type film</td>
<td>2.28</td>
<td>2.31</td>
<td>2.36</td>
<td>2.38</td>
<td>2.43</td>
</tr>
</tbody>
</table>

due to the increase in the ratio of Si/C in these films. The optical bandgap increases gradually with the P concentration in the n-type films [88, 89]. The bandgap increases with the annealing temperature. One can also observe a considerable decrease in the Urbach energy of the p-type films as the doping level increases, while there is almost no change in n-type samples. This is in perfect agreement with the results in [79].

The effects of post-deposition thermal annealing on $E_g$ and $E_{04}$ are summarized in table 4.1 and table 4.2, respectively. Both $E_g$ and $E_{04}$ increase as the anneal temperature and time increase. When annealing in an oxygen ambient, the a-SiC film is oxidized and gradually becomes a mixture of amorphous SiC-SiO. This causes an increase in bandgap as more SiO is formed [90].

**Dielectric constants ($\epsilon_\infty$)**

Figure 4.9 shows the influence of the deposition parameters on the dielectric constant of the a-SiC films. The dielectric constant of the a-SiC films are in
Figure 4.9: Effect of the deposition parameters on dielectric constant of the a-SiC films.

Figure 4.10: Effect of the deposition parameters on (a) $n_{633}$ and (b) $n_0$ of a-SiC films.
the range from 5 to 9. The dielectric constant increases with the temperature and the SiH\textsubscript{4} gas flow rate, while the pressure decreases. The HF and LF components have almost no effect on the dielectric constant of the a-SiC films.

**Refractive index (\(n\))**

Figures 4.10(a) and 4.10(b) report the \(n_{633}\) and \(n_0\) (refractive index at 633nm and at 0nm) of the a-SiC films, respectively. The \(n_{633}\) and \(n_0\) values are in the range from 2 to 3. They increase with the temperature and the SiH\textsubscript{4} gas flow rate, while the pressure decreases. The refractive index of a-SiC films as a function of wavelength has been reported earlier [89].

The refractive index value of samples in an amorphous state is somewhat larger than that of samples in a crystalline state. The large changes in the refractive index indicate differences in the bonding and thus the polarization of the material. Its high infragation index makes PECVD SiC a suitable material for anti-reflection coating, for waveguides or for window of solar cell applications.

**Dispersion energy (\(E_d\)) and oscillator energy (\(E_0\))**

Figures 4.11(a) and 4.11(b) show the influence of the deposition parameters on the dispersion energy and oscillator energy of the a-SiC films, respectively. The dispersion energy is in the range from 20eV to 30eV and strongly affected by temperature. The oscillator energy is only affected by the SiH\textsubscript{4} gas flow rate, and varies in the range from 4eV to 6.5eV.

**Carrier concentration to the effective mass ratio (\(\frac{N}{m^*}\))**

Figure 4.12 shows, the effect of the deposition parameters on \(\frac{N}{m^*}\) of the a-SiC films. The \(\frac{N}{m^*}\) decreases as the temperature and the SiH\textsubscript{4} gas flow rate increase, and for decreasing pressure and LF component.

As mentioned in chapter 2, the statistical tool ANOVA has been used to quantitatively evaluate the effect of deposition parameters on properties of the a-SiC films. Details of this method are presented in appendix A.2. Table 4.3 summarizes the contribution of the deposition parameters to the optical constants of the a-SiC films.

In short, a relationship is established between optical properties of the a-SiC films and the deposition parameters in the PECVD growth process. The SiH\textsubscript{4} flow rate results in sensible changes in the chemical composition of the films and is the most influential deposition parameter. In-situ doping and post-deposition treatments also play an important role in controlling the optical properties of these films.
Figure 4.11: Effect of the deposition parameters on (a) dispersion energy ($E_d$) and (b) oscillator energy ($E_o$) of a-SiC films.

Figure 4.12: Effect of deposition parameters on the carrier concentration to the effective mass ratios of a-SiC films.
Table 4.3: Contributions of the deposition parameters on the optical constants of the a-SiC films.

<table>
<thead>
<tr>
<th>Optical constants</th>
<th>Contributions (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Temp.</td>
</tr>
<tr>
<td>Bandgap ($E_g$)</td>
<td>16.02</td>
</tr>
<tr>
<td>Absorption gap ($E_{04}$)</td>
<td>5.03</td>
</tr>
<tr>
<td>Dielectric constant ($\varepsilon$)</td>
<td>21.10</td>
</tr>
<tr>
<td>Refr. index at 0nm ($n_0$)</td>
<td>41.49</td>
</tr>
<tr>
<td>Refr. index at 633nm ($n_{633}$)</td>
<td>19.39</td>
</tr>
<tr>
<td>Dispersion energy ($E_d$)</td>
<td>55.79</td>
</tr>
<tr>
<td>Oscillator energy ($E_0$)</td>
<td>0.36</td>
</tr>
<tr>
<td>Carrier ratio ($\frac{N}{m^*}$)</td>
<td>14.24</td>
</tr>
</tbody>
</table>

4.3 Electrical properties

4.3.1 Test structures

To evaluate the electrical properties of a PECVD a-SiC film, we fabricated and measured several test structures.

The van der Pauw structure

The van der Pauw test structure is used to determine the sheet resistance of the film, as illustrated in figure 4.13. The measurement is carried out by driving a current through two probes and subsequently measuring the voltage across two other probes. The sheet resistance is given by [91]

$$\rho_s = \frac{\pi}{\ln 2} \times \frac{V_{34}}{I_{12}}$$

(4.19)

where $V_{34} = V_3 - V_4$ is the voltage difference between the two probes 3 and 4, and $I_{12}$ is the current owing into contact $I_1$ and out of $I_2$.

The Metal-Insulator-Metal (MIM) structure

MIM capacitors are valuable in many applications. Figure 4.14 shows the cross section of a MIM structure.

From capacitance measurements between two metal layers in a MIM structure, the dielectric constant $\varepsilon_r$ is calculated using the following formula
Figure 4.13: The van der Pauw test structure.

Figure 4.14: Cross section of a MIM structure.

\[ \varepsilon_r = \frac{C_f t_f}{\varepsilon_0 A} \]  \hspace{1cm} (4.20)

where \( A \) is the area of the electrode (m²), \( t_f \) is the film thickness (m), \( \varepsilon_0 \) is the permittivity of the free space \( (8.854 \times 10^{-12} \text{ F/m}) \), and \( C_f \) is the capacitance of the film (F).

The Metal-Insulator-Semiconductor (MIS) structure

Figure 4.15 shows the cross section of a MIS structure. When the electric field is high enough, the insulator shows carrier conduction. Many types of conductive mechanisms have been proposed. Table 4.4 shows the conduction processes in insulator [92].

From the high-frequency C-V measurements the flatband voltage \( V_{FB} \) has been determined by plotting the \( \frac{1}{C^2} \) versus \( V \) curve and taking the intercept with the \( V \)-axis [91].
Figure 4.15: Cross section of the MIS structure.

Table 4.4: Conduction processes in insulators.

<table>
<thead>
<tr>
<th>Emission type</th>
<th>Expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>Schottky</td>
<td>[ J = A \times T^2 \exp \left( -q \frac{\Phi_B - \sqrt{\frac{qE}{4\pi\varepsilon_i}}}{kT} \right) ]</td>
</tr>
<tr>
<td>Frenkel-Poole</td>
<td>[ J \sim E \exp \left( -q \frac{\Phi_B - \sqrt{\frac{qE}{\pi\varepsilon_i}}}{kT} \right) ]</td>
</tr>
<tr>
<td>Tunnel or field</td>
<td>[ J \sim E^2 \exp \left( \frac{4\sqrt{2m^*(q\Phi_B)^{3/2}}}{3qhE} \right) ]</td>
</tr>
<tr>
<td>Space-charge-limited</td>
<td>[ J = \frac{8\varepsilon_i \mu V^2}{9d^3} ]</td>
</tr>
<tr>
<td>Ohmic</td>
<td>[ J \sim E \exp \left( -\frac{\Delta E_{ae}}{kT} \right) ]</td>
</tr>
<tr>
<td>Ionic conduction</td>
<td>[ J \sim \frac{E}{T} \exp \left( -\frac{\Delta E_{ai}}{kT} \right) ]</td>
</tr>
</tbody>
</table>
The threshold voltage $V_T$ is calculated with the following formula

$$ V_T = V_{FB} + 2\Phi_F + A\frac{(2qK_S\epsilon_0N_A2\Phi_F)^{1/2}}{C_{SiC}}. \quad (4.21) $$

where $V_{FB}$ is the flat-band voltage, $\Phi_F$ is the Fermi potential (V), $A$ is the area (cm$^2$) of the top electrode, $q$ is the magnitude of the electron charge ($1.60 \times 10^{-19}$(C)), $K_S$ is the semiconductor dielectric constant, $\epsilon_0$ is the permittivity of the free space ($8.854 \times 10^{-14}$(F/cm)), $N_A$ is the acceptor density (cm$^{-3}$), and $C_{SiC}$ is the accumulation capacitance (F).

4.3.2 Experimental

Samples preparation

The detailed flowcharts for preparing the van der Pauw, the MIM and the MIS structures can be found in the appendices B.1, B.2 and B.3, respectively.

Rectangular Al/a-SiC/Al capacitors with different areas ($1 \times 10^{-4}$cm$^2$, $6.25 \times 10^{-4}$cm$^2$, $2.5 \times 10^{-3}$cm$^2$, $1 \times 10^{-2}$cm$^2$, and $2.5 \times 10^{-1}$cm$^2$) and a square area of 800μm × 800μm for the Al/a-SiC/Si/Al structure were designed.

The conditions to prepare a wide range of a-SiC films with varying chemical compositions, doping types and thicknesses can be seen in table 2.4.

To investigate the effect of post-deposition laser annealing on electrical properties of the undoped and in-situ doped a-SiC films, we used XeCl$_2$ UV laser ($\lambda = 308$nm) to scan the wafer surface with three shots and ten shots with an overlap of 66% and 90%, respectively. The experiment details of the laser annealing are described in section 2.5.3.

Measurement set-up

The sheet resistance measurements have been performed with an HP 4156B Precision Semiconductor Parameter Analyzer. Current versus voltage (I-V) and breakdown voltage measurements were carried out with an HP 4156B Precision Semiconductor Parameter Analyzer. The upper electrode was biased from 0 to 40V with a step of 0.2V, and the lower electrode was connected to the ground.

The breakdown fields of MIM capacitors were defined by the applied field at which the current exceeds 10nA. The dielectric layer was not destroyed by the breakdown measurements. The perimeter capacitance was less than 1.1%; therefore it is negligible for large capacitance areas. The breakdown field of the
insulator was obtained by plotting the breakdown voltage versus the thickness of the film.

A capacitance versus voltage (C-V) measurement were carried out on an HP 4284A Impedance meter and Cascade Microtech (wafer prober) at room temperature. All measurements were done with the samples placed in an enclosed probe station to screen them from light and electrical noise. The measurements were performed at 100kHz with small-signal bias amplitudes of 15mV (AC signal). To verify that series resistance could not influence the measurement, the capacitance at frequencies of 10kHz, 100kHz and 1MHz were checked. The DC bias voltage was varied from -10 to 40V in a step of 0.2V. In case of the MIM structure, the DC bias voltage was kept at 0V. During these measurements, the top electrodes were negatively biased with respect to the p-type substrates to ensure that the silicon surface was in the accumulation mode and the entire applied voltage appeared across the SiC layer.

4.3.3 Results and discussions

Sheet resistance

Both doped and undoped samples show a sheet resistance of ~ 10^{10} ÷ 10^{11}Ω/□ (sheet resistance of oxide 10^{13}Ω/□). In case of the undoped films, the results show a significant shift in sheet resistance for Si-rich films, while no considerable change is observed for the C-rich films [93].

Table 4.5: Sheet resistance of laser annealed a-Si_{0.54}C_{0.46} films.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Energy</th>
<th>Energy × 10^7</th>
<th>66%</th>
<th>90%</th>
</tr>
</thead>
<tbody>
<tr>
<td>undoped</td>
<td>120</td>
<td>8.54 ± 0.33</td>
<td>8.32 ± 0.57</td>
<td>10^7</td>
</tr>
<tr>
<td></td>
<td>140</td>
<td>7.39 ± 0.09</td>
<td>6.84 ± 0.11</td>
<td>10^7</td>
</tr>
<tr>
<td></td>
<td>160</td>
<td>7.18 ± 0.38</td>
<td>6.18 ± 0.09</td>
<td>10^7</td>
</tr>
<tr>
<td>p-type</td>
<td>120</td>
<td>4.52 ± 4.92</td>
<td>2.71 ± 0.05</td>
<td>10^8</td>
</tr>
<tr>
<td></td>
<td>140</td>
<td>8.36 ± 1.07</td>
<td>2.38 ± 1.27</td>
<td>10^5</td>
</tr>
<tr>
<td></td>
<td>160</td>
<td>1.97 ± 0.13</td>
<td>3.20 ± 0.55</td>
<td>10^3</td>
</tr>
<tr>
<td>n-type</td>
<td>120</td>
<td>3.58 ± 0.04</td>
<td>1.06 ± 0.33</td>
<td>10^8</td>
</tr>
<tr>
<td></td>
<td>140</td>
<td>2.01 ± 0.82</td>
<td>1.26 ± 0.18</td>
<td>10^8</td>
</tr>
<tr>
<td></td>
<td>160</td>
<td>4.97 ± 3.08</td>
<td>1.92 ± 0.28</td>
<td>10^7</td>
</tr>
</tbody>
</table>
Table 4.5 shows the sheet resistance of in-situ doped and undoped films for the various laser annealing conditions used. The sheet resistance decreases as both the energy density and overlap increase. This is related to the activation of the atoms. The lowest sheet resistance achieved on laser annealed n-type doped silicon carbide films is 3.2kΩ/□. The n-type in-situ doped films show a lower sheet resistance than the p-type in-situ doped films when subjected to the same laser annealing treatment. Based on the structural analysis reported in section 3.2.1, it appears that P atoms replace C atoms, while B atoms replace Si atoms. The activated Si content plays an important role in the sheet resistance of the films. Therefore the difference between laser annealed n-type and p-type films is probably related to the Si concentration of the films.

As reported in chapter 3, the structure of an a-SiC film becomes nanocrystalline after a laser annealing treatment. Therefore, in addition to the activation of the Si atom, the change in phase is likely to contribute to the change in electrical properties of the a-SiC films.

The MIM structure

Dielectric constant

Figure 4.16 shows the dielectric constant εr of 500nm a-SiC films with different composition. The values of the dielectric constant between 7.2 ± 0.10 and 8.7 ± 0.22 are found and their dependence on the Si/C atom ratio is clearly observed. The dielectric constant increases with the silicon content, becoming

![Dielectric constant vs SiH$_4$ flow rate](image_url)

Figure 4.16: Dielectric constant of undoped a-SiC films versus SiH$_4$ flow rate.
more pronounced in the region where the film is C-rich. Therefore, when a film with a high dielectric constant \( \varepsilon_r \) is required, the gas flow rate of SiH\textsubscript{4} should be increased. The dielectric constant \( \varepsilon_r \) of a p-type film is slightly lower than that of the undoped film. For n-type films, the dielectric constant cannot be determined due to higher leakage current densities and lower breakdown fields. Both are obtained from the I-V measurements.

**Breakdown voltage**

The breakdown voltage of an Al/a-Si\textsubscript{0.46}C\textsubscript{0.54}/Al capacitor with thickness in the range from 100nm to 900nm were measured. The results show that the breakdown voltage depends linearly on thickness, see figure 4.17.

![Graph showing breakdown voltage versus thickness](image)

**Figure 4.17: Breakdown voltage versus thickness of a-Si\textsubscript{0.46}C\textsubscript{0.54} film.**

The breakdown field of the insulator was obtained by plotting the breakdown voltage versus the thickness of the film. The breakdown field is about 1MV/cm. The breakdown field and the leakage current density for p-type a-SiC films were investigated and compared to those for undoped a-SiC films (see table 4.6).

The low leakage current density (\( \leq 1.2A/cm^2 \)) and the high breakdown field (\( \geq 0.6MV/cm \)) were obtained for the p-type a-Si\textsubscript{0.46}C\textsubscript{0.54} film and undoped C-rich a-SiC films. The structure with the a-Si\textsubscript{0.63}C\textsubscript{0.37} film is more likely to be a resistor because of its high leakage current density and low breakdown field. The undoped and p-type a-Si\textsubscript{0.46}C\textsubscript{0.54} film can be used as an insulating material due to their low leakage current density and high breakdown field. The conductivity increases as the C content in the film decreases.

It can be concluded that when there is the need for high capacitance on
a small area, the p-type doped a-Si_{0.63}C_{0.37} and undoped a-Si_{0.58}C_{0.42} can be used because of their high dielectric constant. For higher Si content, the leakage current density increases substantially, and the layer behaves as a resistor.

The MIS structure

I-V characteristics

Figure 4.18 shows the I-V characteristics of a-SiC films with different compositions at room temperature. A change in the curves of I-V characteristics is observed, indicating a corresponding change in the carrier transport mechanism. The critical value of forward bias voltage increases as the Si/C ratio increases. After a critical value of a forward-bias voltage, the slope of the I-V diagrams of C-rich and Si-rich films changes due to the existence of different transport mechanisms [94].

The conduction mechanism is possibly due to either the Schottky or the Frenkel-Poole effect as both these effects have the same log(σ) versus E^{1/2} dependence. The Frenkel-Poole current mechanism is caused by field-enhanced thermal excitation of trapped electrons into the conduction band, while the Schottky conduction is caused by thermionic emission of charge across the insulator. At higher electric fields, the I-V characteristics show the Frenkel-Poole conduction mechanism for the Si-rich undoped a-SiC films and the Schottky effect for C-rich films. For the p-type doped films, the Frenkel-Poole effect is the only conduction mechanism, while for the n-type films, the behavior is less clear (breakdown field is less than 0.05 MV/cm).

C-V characteristics

The high frequency capacitance versus the gate voltage of the C-rich and Si-rich a-SiC films are shown in figures 4.19(a) and 4.19(b), respectively. For
Figure 4.18: I-V characteristic of a-SiC films with different compositions.

C-rich samples, the C-V curves show typical shape of a MIS structure, which can be described in terms of the accumulation, depletion and inversion regions. In case of Si-rich samples, up to a voltage of 40V, only accumulation and depletion regions appear in the plot. From this figure, we can observe the $V_{FB}$ of the Si-rich film is about 40V.

Figure 4.20 shows the $\frac{1}{C^2}$ versus voltage plots of the C-rich a-SiC films. The $V_{FB}$ of a-Si$_{0.46}$C$_{0.54}$ and a-Si$_{0.32}$C$_{0.68}$ are approximately 7.8 and 10, re-

Figure 4.19: C-V characteristic of a-SiC films (a) C-rich and (b) Si-rich.
spectively. The $V_{FB}$ decreases as the C content decreases. The obtained results show the $V_T$ of a-Si$_{0.46}$C$_{0.54}$ is 10.5V, while $V_T$ of a-Si$_{0.32}$C$_{0.68}$ is 10.8V.

4.4 Concluding remarks

It is clear that the optical and electrical properties of a-SiC films prepared by the PECVD technique make this material a promising candidate for many opto-electronic applications. The considerable changes in the optical properties of the films obtained by varying the deposition parameters, and by doping and thermal annealing could potentially be of interest for the recently developed MOEMS devices, for example for waveguides. These applications will be discussed in chapter 6.

Because of its very high sheet resistance, the applications of a-SiC films for capacitor sensors are considered. Lowering the sheet resistance of these films is a difficult problem, for which the laser annealing technique offers a possible solution. The initial results indicate that this technique is beneficial for p-type films as the resistance can be reduced from $10^{10}$Ω/□ to $10^3$Ω/□. For some applications, further investigation on the effect of this technique for other properties of a-SiC films might be required, for example the optical and mechanical properties.
Chapter 5

All-dry post-processing surface micromachining module

5.1 Introduction

The most important requirement for the sacrificial layer is that it must be quickly etched with high selectivity to the layers between which it is sandwiched [8]. A wide range of materials, briefly reviewed in section 5.2, have been used for the sacrificial layer.

Regardless of the materials, the stiction problem that is related to the use of a wet etch step to release the microstructures is a major concern in many surface micromachining processes developed so far [95]. Existing methods for stiction prevention often require complicated systems, specific chemicals and additional rinsing steps. Section 5.3 gives a brief review on mechanisms causing stiction and current approaches to prevent stiction in micromachining.

Among the recently proposed materials, polyimide is a potential candidate for the sacrificial layer in post processing surface micromachining technology, since the preparation, patterning and releasing steps can be carried out at low temperature. Polyimide is also a suitable sacrificial layer for several structural layer combinations, as both isotropic and anisotropic O$_2$ plasma etchings are possible for the patterning and releasing steps, respectively. Moreover, polyimides offer additional advantages: (i) they are relatively low-cost materials, (ii) the fabrication is quite simple, as no high-temperature processes are needed, and (iii) they can be deposited on various type of substrates [96].

In this chapter, the possibility of using polyimide as a sacrificial layer for
surface micromachining technology will be investigated. We present a fully IC-compatible all-dry post-process module, developed to preserve flexibility without increasing process complexity. This new module overcomes the stiction problem by using an all-dry release step, followed by a final dry cleaning step. This means that no fluid is employed to free the structure and therefore no wet cleaning and complex drying steps are necessary.

5.2 Materials for sacrificial layers

The sacrificial material is required to have good uniformity and proper mechanical properties, e.g., good adhesion and low residual stresses, so as not to cause device failure during the fabrication process. They must also withstand the processing conditions required for the subsequent structural and sacrificial layers. The chemical etchants, which are utilized to fully release the sacrificial layer, must be able to preferentially etch the sacrificial material with respect to the structural parts and underlying integrated devices or circuitry [7]. The following materials have been used as sacrificial layers in surface micromachining.

5.2.1 Insulating materials

- Silicon dioxide (SiO$_2$): Silicon oxide is a viable sacrificial film for polysilicon surface micromachining due to the excellent properties, namely no cracking and minimal warpage during thermal processing, and high conformality. The possibility of selectively etching oxide layers with respect to Si during the final release etch without jeopardizing film stability is a major technological step in surface micromachining processes [97].

- Phosphosilicate glass (PSG): PSG is one of the most suitable sacrificial layers due to its low deposition temperature, high etch rate and etch selectivity to several commonly used structural layers. The high etch rate of the PSG is mainly due to the presence of phosphorus. However, the disadvantages of PSG sacrificial layers are their poor uniformity, outgassing of phosphorus at high temperature and structural modification of the layer during thermal processing. Heat treatment leads to shrinkage and etch rate reduction. Considering this effect, the sacrificial layer requires a thermal treatment to pre-shrink the layer prior to the structural layer deposition [98, 99].

- Photoresists (PR): PR has been used as a sacrificial layer as they have a number of advantages, such as the ease with which (i) resist coating
can be applied on a wafer, (ii) the resist layer can be dissolved in a benign solvent solution that does not hurt the fabricated circuitry, and (iii) the resist layer thickness can be controlled. In addition, the use of photoresist may require a fewer number of fabrication masks and hence a smaller number of processing steps, thereby improving process yield and reducing cost [45, 100].

5.2.2 Semiconducting materials

- Polysilicon (Poly-Si): Since poly-Si is a compatible material for integrating MEMS with on-chip electronics, not only is it used as a structural layer but also as a sacrificial layer. It can be etched using etchants traditionally used for bulk micromachining, for example, EDP, KOH and TMAH. Many materials, including SiO$_2$ and SiN often used to stop etching Si, can be used as a structural layer while using Si as sacrificial layer due to their high selectivity with Si in these solutions [101, 102].

- Porous silicon (PS): PS possesses many attractive features making it a very interesting material as a sacrificial layer with a wide range of thicknesses (up to 100$\mu$m or thicker). A PS sacrificial layer has many advantages over commonly used SiO and PSG layers (i) it can be generated locally using different doping levels as well as appropriate masking, (ii) it can be quickly and easily removed with a very weak KOH solution and at ambient temperature, and (iii) PS formation is CMOS compatible, requiring little processing time and inexpensive processing equipments [103, 104, 105].

- Germanium (Ge): For applications of Ge as a sacrificial material, two general wet etchants, HNO$_3$:$H_2$O:HCl=5:3:3 and H$_2$O:H$_2$O$_2$:HCl=4:3:1, have been developed [37]. A number of gas phase techniques, including thermal treatment in TCA or in N$_2$ ambient with a trace amount of O$_2$ and vacuum evaporation with an extremely low O$_2$ partial pressure, have been successful tested. However, its use in surface micromachining has not yet been implemented.

- III-V compounds (III-Vs): Epitaxy of III-Vs compounds provide a variety of well-defined layer thicknesses and stresses, as well as several layer combinations facilitating sacrificial layer etching. Sacrificial etching of III-Vs is frequently used in lift-off epitaxy, transferring an epitaxial layer of III-Vs to other host substrates [106, 107].
5.2.3 Conducting materials

- Metals: Electroplated metal layers with several microns in thickness have been used as sacrificial materials to achieve large gaps between surface micromachined structures and substrates. Al is considered as a sacrificial layer only for low temperature process due to its melting point. Combined with chemical inert metals like Au or Ni, commonly used in microsystem technology, Cu or Zn can also be used as sacrificial materials [108, 109, 110].

5.3 The stiction problem

The stiction problem occurs when surface adhesion forces are higher than the mechanical restoring force of the microstructure (see figure 5.1). This phenomenon is one of the major obstacles that slow down development of surface micromachined devices. It may occur either during the final steps of the micromachining process (release stiction) or after the device packaging due to overrange input signals or electromechanical instability (in-use stiction) [111].

![Diagram of the stiction problem](image)

Figure 5.1: The stiction problem: (a) before sacrificial etching, (b) beginning of drying stage, (c) capillary forces acting on the cantilever, and (d) cantilever stuck to the substrate.

Here we address stiction during fabrication. A number of experimental techniques have been developed to prevent the stiction phenomenon of the surface micromachined structures during release and drying steps. In order to alleviate these problems, both the topography and the chemical composition of the contacting surface must be controlled.
5.3.1 Adhesion forces

Understanding of the stiction phenomenon is important for applications of surface micromachined structures with respect to technological realization and other tribological aspects. Studies have reported that capillary, electrostatic and van der Waals forces, and in some cases "chemical" forces such as hydrogen bonding and solid bonding are mainly responsible for the stiction problem. These forces can be quantified to varying degrees, with theoretical analysis providing insights into directions for minimizing stiction [112, 113].

Figure 5.2 compares surface forces acting on a microstructural element during post-release drying. The graph indicates that the capillary force attraction is greater than both electrostatic and van der Waal forces [9].

![Graph showing comparison of surface forces acting on a microstructural element during post-release drying.](image)

Figure 5.2: Comparison of surface forces acting on a microstructural element during post-release drying.

**The capillary force**

The capillary force results from trapped liquid, which produces an attractive force due to Laplace pressure differences and surface tension forces. All models of capillary forces recognize the influence of surface chemistry as manifested by contact angles. The presence of the liquid is either a product of the release process or a result of humidity. To calculate the capillary force we have to consider both situations.
The surface tension of the diminishing liquid induces an attractive capillary force, which is inversely proportional to the gap spacing between the microstructure and the substrate, see figure 5.3.

![Cross section of the microstructure during drying.](image)

Figure 5.3: Cross section of the microstructure during drying.

The capillary force $F_p$ is derived from the stiction theory

$$F_p = \int_{\delta}^{\infty} -\frac{\gamma(\cos \theta_1 + \cos \theta_2)}{\delta} d\delta$$

(5.1)

where $\gamma$ is the surface tension of the liquid, $\theta_1$ and $\theta_2$ are the contact angles of the liquid with the two surfaces, and $\delta$ is the gap between the structural layer and the substrate.

**The van der Waals force**

The van der Waals force is the basic quantum mechanical inter-molecular force that results from the interaction between instantaneous dipole moment of atoms. When working with very planar crystalline structures, as in MEMS, these forces can be very significant.

There are two methods to calculate the van der Waals attractive force between solids, the microscopic and macroscopic approaches. The former starts from the interaction between individual atoms and molecules, postulates their additivity so that the force can be calculated by integration over all pair of atoms and molecules. The latter starts directly from optical properties of the interacting macroscopic bodies and can be calculated from the imaginary part of their complex dielectric constants, especially their far ultraviolet portion.

The interaction force per unit area due to van der Waals interaction is given by:

$$F_{vdW} = -\frac{A}{12\pi d^2}$$

(5.2)

where $A$ is the Hamaker constant and $d$ is the distance between the surfaces. For most solids and liquids, the Hamaker constant lies in the range $0.4 \div 4 \times 10^{-19}J$ [114, 115].
The electrostatic force

Electrostatic forces are the result of the Coulombic attraction that often results from trapped electric charges. It is almost impossible to calculate this force because of the incomplete knowledge of the electrical properties of the material involved; especially the electronic energy spectrum of the surface is practically unknown for almost all materials. Neglecting the internal space charge regions, the acting force is given by

$$F_{el} = \frac{\varepsilon_0 U^2 A}{2\delta}$$  \hspace{1cm} (5.3)

where $U$ is the potential difference between the surfaces separated by an air gap $\delta$ with permittivity $\varepsilon_0$, and $A$ is the shared area of the parallel surfaces [112, 116].

Hydrogen bonding

Hydrogen bonding represents one of the most important forms of molecular interaction. It exists between two highly polar molecules containing hydrogen. The simple explanation of this mechanism is as follows. A hydrogen atom has a relatively low electronegativity (2.2), and when it is covalently bonded to other atoms with higher electronegativity (e.g., $\chi_O = 3.5$), the resulting bonds are polar. When two such molecules are nearby, they will orientate themselves so that the partially negative end of one molecule will face the partially positive end of another molecule, resulting in a hydrogen bond.

In surface micromachining, the hydrophilic surfaces of both the substrate and the structural layer contain a large number of hydroxyl groups. The hydroxyl group can form a strong hydrogen bond as the separation between both surfaces becomes small [117].

Solid bonding

This phenomenon usually occurs when the drying step is carried out by means of an evaporation method. Non-volatile impurities, present either in the drying liquid or through dissolution of the particles and/or substrate materials in the liquid, are deposited on solid surfaces. Because deposition is pronounced in narrow spaces and between contacting surfaces, cementing the structural layer and substrate happens.

The formation of covalent bonds between two surfaces is similar to the process of wafer bonding. The adhesive strength resulting from solid bridging
is difficult to estimate because of the variability in the deposition process and the density of the deposited material [117, 116].

5.3.2 Anti-stiction methods

A number of experimental techniques have been developed to prevent the stiction problem. Common approaches to reduce adhesion in microstructures are coating, rough surface and drying process are presented below.

Anti-stiction coatings

One attractive approach to tackle the stiction problem is to provide a low-energy surface coating in the form of an organic passivation layer on the inorganic surface. Due to the hydrophobicity of such coating, not only can capillary forces and direct chemical bonding be eliminated or reduced, but also the electro-static forces can be reduced. However, in view of the critical importance of anti-stiction coatings in MEMS products, they must possess the following attributes (i) the chemistry is simple and reproducible, (ii) the coatings are of monolayer nature and are covalently bonded to the substrate, (iii) the coating processes are compatible with dry or aqueous etching processes, and (iv) the monolayers are chemically and mechanically stable under processing and operation conditions. This method requires no sophisticated instrumentation, but many chemical and rinsing steps.

![Diagram of SAM coating process to prevent stiction phenomenon.](image)

Figure 5.4: A SAM coating process to prevent the stiction phenomenon.

Self-assembled monolayer (SAM) coatings

SAM coating is a promising technique to reduce both release and in-use stiction in micromachined devices. It can be prepared using different types of molecules and different substrates. A molecule which is essentially an alkane chain, typically with 10-20 CH₃ units, is given a head group that reacts with hydrophilic
Si surfaces, and a tail group that increases the hydrophobicity of the Si surface (see figure 5.4). Some SAM coatings, derived from the precursor molecules octadecyltrichlorosilane (OTS), 1H, 1H, 2H, 2H-perfluorodecyltrichlorosilane (FDTS) or n-decyltrichlorosilane (DTS), have been successfully applied to fabricate MEMS [118, 119].

Alkene based monolayer coatings

Alkene based monolayer coating, a new class of anti-stiction coating for poly-Si MEMS, has shown certain advantages over SAM coatings. It abandons the chlorosilane chemistry and adopts a free radical reaction of a primary alkene to bind the precursor molecules to a hydrogen terminated Si substrate. Additionally, there is no need for oxidation of the surface, since the molecule binds directly to the Si. The coating procedure is insensitive to ambient humidity. The primary alkene is very stable at room temperature, and hence the coating solution can be stored indefinitely [120].

Drying process

The major cause of permanent stiction is the surface tension at the interface between liquid and air during the drying process followed by the wet etching of the sacrificial layer. After a device has gone through the sacrificial etch step, a common way of alleviating or removing the stiction problem is to use drying processes, which transfer water or solvent from liquid into vapor phase during the drying step. Figure 5.5 shows the phase diagram to apply for various drying processes. There are three main methods: evaporation drying (path liquid → vapor), sublimation drying (path liquid → solid → vapor) and supercritical drying (path liquid → critical point → vapor) [113].

Evaporation drying

In this method, long rinse in high quality DI water helps reduce the accumulation of residual particles under the released microstructures and the effect of solid bringing. Since the molecular kinetic energy gets higher as the temperature increases, more molecules can escape the surface and the saturated vapor pressure gets higher correspondingly. As a result, an elevated temperature is required. On the other hand, other low surface tension solvents (e.g., methanol and isopropanol) can be used to replace DI water in the last step. While this method is simple, the results are not impressive [113].

Sublimation drying

In principle, referring to the phase diagram (see figure 5.5), sublimation drying of water or solvent is taking place at low temperature and pressure. The freeze-
dry process is divided into two different physical process steps. Step one is the freezing of the water or solvent below its solidification temperature, and step two removes the ice or solvent crystals at a very low temperature. The disadvantage of this method is the toxicity of the solvents used [113].

Supercritical drying

The principle of these methods is to transfer water or solvents from liquid to vapor through a supercritical state. The application of CO₂ solvent extraction to surface micromachined structures was demonstrated as an effective drying technique. Since a liquid-vapor interface is not formed, capillary forces are unable to bring adjacent surfaces into contact with one another and stiction was not observed. This method is clean and produces excellent results. However, it requires a complicated and costly apparatus [113].

Dry release methods

Isotropic dry etching that releases the sacrificial layer at the final stage of the fabrication processes is an attractive alternative to the above methods for stiction prevention; because no liquid is involved and excellent results are obtained. A disadvantage is that they often require dedicated or not fully developed equipment.

HF vapor phase etching
The possibility of stiction free etching, as well as high selectivity toward metals makes the HF vapor phase technique an attractive SiO sacrificial etching. This process features simplicity, negligible residues and is compatible to a cluster tool for process integration in the future. This process also has an economic merit of high wafer through-put as in the case of a MEMS device [121, 122]. The overall chemical reaction for SiO$_2$ using HF vapor phase is:

$$\text{SiO}_2(s) + 4\text{HF}(g) \rightarrow \text{SiF}_4(g) \uparrow + 2\text{H}_2\text{O}(g) \uparrow$$

The products of SiF$_4$ and H$_2$O are removed from the oxide surface by desorption during heating.

**XeF$_2$ vapor and plasma etching**

Using XeF$_2$ either in vapor phase or in reactive ion etching is a cost-effective isotropic etching of Si and the solution for MEMS release when silicon is used as a sacrificial layer due to the high selectivity with respect to Al, photoresist, and SiO [123]. The following chemical reaction occurs between XeF$_2$ and Si in an etching process

$$\text{Si}(s) + 2\text{XeF}_2(g) \rightarrow 2\text{Xe}(g) \uparrow + \text{SiF}_4(g) \uparrow$$

The products of Xe and SiF$_4$ are easily pumped away, which completes the etching process.

**O$_2$ based plasma etching**

Photoresists (PR) and polyimide (PI) are known as traditional microelectronic materials. They can be removed using an O$_2$ plasma which does not affect any other IC layer. The use of an organic layer as a sacrificial layer and O$_2$ plasma as removal have been demonstrated and are especially attractive for compatibility of MEMS with conventional IC processes [100, 124].

Like other organic materials, after fully ashing in O$_2$ plasma, the final products of this process are CO$_2$ and H$_2$O

$$\text{PR}/\text{PI}(s) + \text{O}_2(g) \rightarrow \text{CO}_2(g) \uparrow + \text{H}_2\text{O}(g) \uparrow$$

**Other methods**

Novel processes have been proposed to prevent stiction in specific cases. They include (i) changing the sequence of the sacrificial etching, (ii) silicon selective
etching, and (iii) releasing the polymer used for replacing etchant after etching the sacrificial layer in successive steps in O₂ plasma. Details of these methods as well as their advantages and disadvantages can be found in [125, 126, 127].

5.4 Polyimide as a sacrificial layer

Polyimides have been used widely in microelectronics, in multilevel electronic structures as an interlayer dielectric or in multilayer resist systems to planarize bottom layers, because they possess excellent process resistance, good planarization, step-coverage abilities and dielectric properties. Polyimides in MEMS technologies have been receiving increasing attention as they exhibit unique mechanical, chemical and thermal properties [128, 96].

5.4.1 Preparation of polyimide

Commercial polyimide (HD Microelectronics, PI2610) has been selected since it can be easily spun on several microelectronic materials, and it has a transition-to-glass (TG) temperature above the post-processing limit temperature of 400°C. PI2610 is a fully aromatic polyimide based on biphenyldianhydride - 1,4phenylenediamine (BPDA/PPD) backbone chemistry. Figure 5.6 shows the chemical structure of PI2610 polyimide.

![Chemical structure of polyimide PI2610.](image)

Polyimide layers with a thickness of 1-4μm are spun on Si wafers. The promoter VM651 is used to provide good adhesion to the substrate. A delay of 5-6 seconds is allowed prior to spinning to let the polyimide relax and flow on the silicon surface. A spin speed of 2000-6000 rpm is used with a fixed spin time of 30 seconds. Two step baking, 90°C for 3 minutes and 180°C for 90
5.4. Polyimide as a sacrificial layer

![Graph showing polyimide thickness versus spin speed before and after baking.](image)

Figure 5.7: Polyimide thickness versus spin speed before and after baking.

seconds, have been selected in order to get rid of part of the solvent, thus to stabilize the film. The curing is done in an N₂ atmosphere at a temperature of 400°C for 30 minutes. Although polymerization starts at about 200°C, higher baking temperatures are preferred as they allow a complete solvent evaporation and yield a higher TG temperature of the cured polymer. The polyimide layer thickness is measured by ellipsometry, prior to and after the curing step. Figure 5.7 shows the thickness of polyimide prior to and after baking as a function of the spin speed. The average shrinkage due to curing is about 20% of the film thickness for the conditions used. The roughness of polyimide is about 60Å.

The resistance of polyimide to some of the solvents commonly used for cleaning the wafer in between process steps or for removing some layers, such as aluminum, has been tested. Fully cured polyimide is not damaged in a 65% HNO₃ solution at 105°C (inorganic contamination cleaning) or in a 0.55% HF solution (aluminium wet etch). Since polyimide is an organic polymer, it is not resistant to 100% fuming acid.

5.4.2 Dry etching of the polyimide

The polyimide layer needs to be patterned with a reasonable anisotropy to define the sacrificial areas. Moreover, after stripping of the mask layer and deposition of the mechanical layer, a fast highly isotropic etch process is necessary to release the microstructures. Therefore, two types of dry etching process, as depicted in figures 5.8(a) and 5.8(b), have to be developed. Polymer patterning by reactive ion etching (RIE) in O₂ plasma is one of the basis methods used for multilayer resist system fabrication due to the combined
effect of ion and chemical etching mechanisms, providing simultaneously di-
rectionality and high etch rates. Ion bombardment assists etching by driving
off hydrogen and partially oxidize carbon group (C-O, C=O, C-O-C) in the
polymer [128].

Figure 5.8: Schematic drawing of the (a) anisotropic and (b) isotropic etching
of polyimide.

A commercial RF parallel plate system is used in the RIE experiments.
O₂ is used as the etchant gas. All RIE experiments are performed at pressure
of 0.05mbar, power of 60W at room temperature. SiO has been selected as
a hard mask layer for patterning due to its good adhesion to the polyimide
and the ease to remove afterwards. The etch rate determined by measuring
a step with a profilometer (DEKTAK 8, Veeco) is about 217nm/min. in a
gas flow rate of O₂ of 50sccm. SEM images of the profile and etched surface
morphology of polyimide can be seen in figures 5.9(a) and 5.9(b). The etch
rate reaches 350nm/min. at a flow rate of 100sccm. The change in surface
roughness in the O₂ plasma RIE step is not significant.

A mask with different size of holes and trenches has been used to investigate
the under etch rate of polyimide in O₂ plasma. Figure 5.10 shows optical
images of the etch rate of polyimide in O₂ plasma etching. The under etch
rate of the polyimide layer in the plasma condition used is about 4μm/min.

In short, polyimide is a suitable sacrificial layer for MEMS applications. It
highly benefits from an all-dry etching post processing surface micromachining.
Figure 5.9: SEM pictures of (a) anisotropic and (b) isotropic polyimide.

Figure 5.10: Optical images of polyimide under etch rate in O₂ plasma etching.

5.5 An all-dry post-processing surface micromachining module

In this section, an all-dry post-processing surface micromachining module fully compatible with IC conventional processes is introduced. The compatibility of a low tensile stress PECVD SiC film as a structural layer and polyimide as a sacrificial layer provides designers with the possibility to realize micromechanical structures for sensing or actuating in harsh environments. Different kinds of test structures were fabricated to evaluate the feasibility of this module.
5.5.1 A surface micromachining module

Figure 5.11 shows the process flow of an all-dry post-processing surface micromachining module. The detailed process to produce the free-standing microstructure using this module is given in appendix B.5.

1) Spinning and curing polyimide on a Si substrate.

2) PECVD SiO₂ deposition, photoresist coating and patterning with a sacrificial mask.

3) Anisotropic patterning polyimide with a PECVD SiO₂ hard mask in O₂ plasma.

4) Removing PECVD SiO₂ with a HF 0.05% solution.

5) PECVD SiC deposition and patterning to create the microstructures.

6) Isotropic releasing polyimide in O₂ plasma to realize the free-standing microstructures.

Figure 5.11: A schematic view of the cross section of an all-dry post processing surface micromachining module.

5.5.2 Realization of microstructures

A mask set containing cantilever beams, membranes, rotating structures and pointer structures is applied to evaluate the potential of polyimide as a sacrificial layer and silicon carbide as a structural layer. Figures 5.12(a-d) show the SEM pictures of fully releasing PECVD SiC microstructures. This design enables the examination of the following material characteristics

- Mechanical strain using the pointer structures.
Figure 5.12: SEM pictures of test structures. (a) Vernier structure, (b) diamond structure, (c) rotator structure and (d) suspended structure.

- Under etch rate using the tunnels and etch holes of different sizes and configurations.

5.6 Concluding remarks

Among the possible materials for sacrificial layers in surface micromachining, polyimide is a new interesting choice. Especially, it offers the possibility to use an all-dry release step and a full compatibility with the PECVD layers SiO$_2$ and SiC, which is advantageous for a large number of microstructures operating in harsh environments. Several surface micromachined devices employing this module will be discussed in chapter 6.
Chapter 6

Applications

6.1 Introduction

As shown in previous chapters, SiC films prepared by the PECVD technique possess many attractive properties, including the ability to operate at high temperature and chemical inertness in a number of liquid electrolytes. Furthermore, the mechanical, optical, and electrical properties of the material can be controlled by changing the deposition parameters as well as by post-deposition treatment (e.g., doping and annealing). Therefore, this material can be used for many applications in optoelectronics, microelectronics and MEMS and is especially attractive for applications in harsh environments.

In this chapter, we show the potential of SiC films to realize IC-compatible devices. We also demonstrate the attractiveness of the all-dry post-processing surface micromachining module for integrating MEMS devices with on-chip electronics. This work was performed in collaboration with three research projects in DIMES.

Section 6.2 presents three devices that are fabricated using surface micromachining techniques, namely switches, pressure sensors, and vertical accelerometers. These devices, designed by L. Pakula et al. [129, 130], employ the low tensile stress PECVD SiC film obtained by the results reported in chapter 3. The main characteristics of these devices are introduced and discussed.

Section 6.3 presents two other applications of PECVD SiC films, namely a Mach Zehnder interferometer and a humidity sensor. The former, designed by G. Pandraud [131], takes advantage of the high refractive index of PECVD SiC films. The latter, designed by E. Connolly [132], is a novel device that demonstrates the possibility of making these SiC films highly porous, which
results in a large-sensitivity humidity sensor.

6.2 Surface micromachined PECVD SiC microstructures

6.2.1 Electrostatic switch

Three major types of actuation mechanisms that have been extensively investigated are electrostatic, magnetic and thermal actuators. Among them, electrostatic actuation is a popular choice for switches when low displacements are required. In addition, electrostatic actuation is commonly used in MEMS devices because of the simplicity in design, fabrication and operation [133]. In this section, we present a SiC electrostatically actuated microswitch using an all-dry post-processing surface micromachining module.

Experimental

Figure 6.1 shows a schematic concept of an electrostatic actuated switch. The device consists of a cantilever beam, a fixed driving electrode and a mass at the tip of the beam. Bumpers are placed to prevent the beam from making contact with the driving electrode. In the design used for moving elements, there are two types of SiC cantilever beams with a width of 1μm and 2μm, both having a thickness of 1μm and a length of 200μm. The size of the mass is 30μm×30μm; the distance between the driving electrode and the tip of the beam is 15μm; and the size of the beam electrode is 100μm×87μm.

![Schematic view of an electrostatic actuated switch](image)

Figure 6.1: A schematic view of an electrostatic actuated switch.

The structures are fabricated using a three-mask process based on an IC-compatible surface micromachining process, see figure 6.2. In appendix B.6 the detailed flow chart to prepare the microswitch is given.
a) Spinning, curing and patterning polyimide on a Si substrate.

b) PECVD SiC deposition and patterning to create the microswitch.

c) Al sputtering and patterning to make electrodes.

d) Isotropic releasing polyimide in O₂ plasma to realize the freestanding microswitch.

Figure 6.2: A schematic view of the cross section of the all dry post processing surface micromachining module for producing microswitches.

The structure is simulated using the finite element program ANSYS. Because the Young modulus of this film is approximately 460GPa (see section 3.3.3), we use this value in our simulation. The fabricated actuators are tested using an HP 4156B Precision Semiconductor Parameter Analyzer, which can apply a voltage up to 200V. The measurement is performed with two probes; the cantilever beam is grounded with one probe while the DC voltage is applied on the driving electrode with the other probe.

Results and discussions

Table 6.1 gives an overview of the various parameters extracted from the simulation results. A minor increase in the displacement is observed when the voltage between the beam and the driving electrode is increased beyond the pull-in regime.

By applying a voltage of 200V, a displacement of approximately 5μm is measured for the 2μm-wide beam. Compared to the simulated value, this value is slightly higher corresponding to this configuration. This might be the result of the effect of the preparation process on the properties of the SiC film.

In brief, SiC electrostatic actuated switches are successfully realized using the all-dry surface micromachining technique. Furthermore, one could make this device suitable for, for example, switching a light on/off by depositing a
Table 6.1: The simulation results of the switches with 1μm and 2μm wide beams.

<table>
<thead>
<tr>
<th>Beam width (μm)</th>
<th>Pull-in voltage (V)</th>
<th>Displacement (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>90</td>
<td>5.1</td>
</tr>
<tr>
<td>1</td>
<td>95</td>
<td>17.1</td>
</tr>
<tr>
<td>1</td>
<td>100</td>
<td>17.3</td>
</tr>
<tr>
<td>2</td>
<td>200</td>
<td>3.0</td>
</tr>
<tr>
<td>2</td>
<td>235</td>
<td>19.3</td>
</tr>
<tr>
<td>2</td>
<td>240</td>
<td>20.3</td>
</tr>
</tbody>
</table>

refractive material that reacts to light on the surface of the mass at the end of the beam.

6.2.2 Pressure sensor

Pressure is one of the most frequently measured quantities. In automotive, industrial, consumer or medical applications pressure sensors with various requirements are in use. Recently, there has been a trend to use surface micromachined capacitive pressure sensors thanks to their advantageous features such as the small size and the capability to integrate on-chip electronics to miniaturize systems [129]. In this section, we present a capacitive SiC pressure sensor compatible with IC processes using a post-processing surface micromachining technique.

Experimental

The sensors are designed in three sizes to investigate the fabrication process (see table 6.2). The circular shape of membranes ensures no stress concentration at corner points, which often occurs for square membranes.

Table 6.2: Configuration of the capacitive SiC pressure sensors.

<table>
<thead>
<tr>
<th>No</th>
<th>Diaphragm (μm)</th>
<th>Capacitance (pF)</th>
<th>Number of membranes</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>80</td>
<td>14</td>
<td>100</td>
</tr>
<tr>
<td>2</td>
<td>110</td>
<td>18</td>
<td>64</td>
</tr>
<tr>
<td>3</td>
<td>150</td>
<td>33</td>
<td>49</td>
</tr>
</tbody>
</table>
a) Al sputtering and patterning to make the bottom electrode.

b) Polyimide sacrificial layer: spinning, curing and patterning.

c) First PECVD SiC deposition, patterning.

d) Al sputtering and patterning to form the top electrodes.

e) Second PECVD SiC deposition and patterning.

f) Window opening to etch the sacrificial layer.

g) Isotropic releasing polyimide in O₂ plasma to realize the freestanding membranes.

h) Sealing the SiC layer.

Figure 6.3: A schematic view of the cross section of the all-dry post processing surface micromachining module to produce a pressure sensor.

The process to prepare the pressure sensors is illustrated in figure 6.3. The detailed flow chart can be seen in appendix B.7. Since a structural SiC layer is used, no additive protection layer has to be applied.

The sensor is placed in a pressure chamber and connected to a readout circuit. The sensors are measured at pressures from atmosphere down to
100mbar and up to 5bar. For the measurements in vacuum, a SX15AD2 SenSym pressure sensor is used as a reference sensor. The pressure inside chamber is controlled by a DPI 520 sensor calibration setup manufactured by “Druck”. The driving voltage is 1V (AC) with a frequency of 1MHz.

Results and discussions

A SEM image of a completed device is shown in figure 6.4. Figure 6.5(a) and 6.5(b) show the response of a sensor, due to pressure changes from 1bar down to 100mbar and in the range of 1bar to 5bar, respectively.

![SEM image of a surface micromachined pressure sensor.](image)

Figure 6.4: A SEM image of a surface micromachined pressure sensor.

![Graphs showing relative change of capacity versus applied vacuum.](graphs)

Figure 6.5: Relative change of capacity versus applied vacuum (a) in range of 1bar down to 100mbar and (b) in range of 1bar to 5bar.

The change of pressure in a range from 100mbar to 1bar causes a change of capacitance from 14.9pF to 15.3pF. The sensitivity measured is 0.32pF/bar,
compared to the calculated sensitivity of 0.45pF/bar. The linearity in the full pressure in range from 100mbar to 1bar is less than 2%. The change of the pressure in range from 1bar up to 5bar is 3pF.

Measurement values of fabricated devices are similar to values obtained from FEM simulation, as can be seen in table 6.3.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Calculated value</th>
<th>Measured value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capacitance (pF)</td>
<td>13.6</td>
<td>14.9</td>
</tr>
<tr>
<td>Sensitivity (% /bar)</td>
<td>3</td>
<td>2.6</td>
</tr>
</tbody>
</table>

It is concluded that the sensor demonstrates a great promise for many applications because of its high sensitivity and easy integration. Low tensile stress SiC films make this device easier in process. This module has also been applied for low stress PECVD SiN - an IC-compatible material for post-processing surface micromachining. However, the SiN pressure sensor has shown a very high hysteresis response.

6.2.3 Vertical accelerometer

Accelerometers are another typical application of surface micromachined sensors. These sensors are well suited for a wide range of applications, such as vibration monitoring, motion control and inertial guidance. In this section, we report a 3D SiC vertical accelerometer that measures acceleration or gravitational force through a change in capacitance resulting from the motion of a proof mass.

Experimental

The mass of the membrane consists of three layers SiC-Al-SiC suspended on four double layer SiC-Al springs. The bottom electrode is divided in four parts, which enables the canceling of the measurement error introduced by cross-sensitivity. Important parameters of the structure are listed in table 6.4.

Figure 6.6 shows a process to prepare a vertical accelerometer. The detailed flow chart is described in appendix B.8.
Table 6.4: Parameters of the structure of the vertical accelerometer.

<table>
<thead>
<tr>
<th></th>
<th>Length (µm)</th>
<th>Width (µm)</th>
<th>Thickness</th>
</tr>
</thead>
<tbody>
<tr>
<td>Beam</td>
<td>200</td>
<td>2.5</td>
<td>1.8µm SiC + 1.4µm Al</td>
</tr>
<tr>
<td>Mass</td>
<td>500</td>
<td>500</td>
<td>1.8µm SiC + 1.4µm Al + 1.8µm SiC</td>
</tr>
</tbody>
</table>

a) Al sputtering and patterning to make the bottom electrode.

b) PSG as a sacrificial layer depositing and patterning.

c) First PECVD SiC deposition and patterning.

d) Al sputtering and patterning to form the top electrodes.

e) Second PECVD SiC deposition and patterning.

f) Isotropic releasing PSG in 73%HF with the addition of IPA to realize the freestanding membranes. To prevent stiction, a free drying step is applied.

Figure 6.6: A cross-section schematic process to produce a vertical accelerometer.

Results and discussions

The electrical and mechanical properties of the device have been calculated with an analytical model and simulated with ANSYS (see table 6.5).

Figure 6.7 presents a fully released structure of a vertical accelerometer.
Table 6.5: Mechanical and electrical properties of the vertical accelerometer.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resonant frequency</td>
<td>5.6kHz</td>
</tr>
<tr>
<td>$C_0$</td>
<td>0.58pF</td>
</tr>
<tr>
<td>$\Delta C$</td>
<td>1.84fF/g</td>
</tr>
<tr>
<td>Pull-in voltage</td>
<td>3.1V</td>
</tr>
<tr>
<td>Thermal noise</td>
<td>$47\mu g/\sqrt{Hz}$</td>
</tr>
</tbody>
</table>

The initial capacitance is measured to be 0.42pF. The characteristic of the sensor is illustrated in figure 6.8. A good linearity of the vertical accelerometer over the full designed acceleration range from 0.4(g) to 14.4(g) is observed.

Figure 6.7: A SEM image of a fully released vertical accelerometer.

Figure 6.8: Output signal versus accelerations.
The described vertical accelerometer using PECVD SiC films can be integrated with a standard IC process. This process is now being considered to prepare 3D lateral accelerometers [130].

6.3 Other possibilities of PECVD SiC films

6.3.1 Mach Zehnder interferometer

Mach Zehnder interferometers are used to prepare difference signals and optical routing-switching in optical signal processing, for example in the field of optical sensing and high capacity optical networks. PECVD SiC with a high refractive index is a suitable material for passive optical component such as waveguides, couplers and interferometers [131]. This section demonstrates basic Mach Zehnder interferometers fabricated with a high refractive index PECVD SiC films on Si.

Experimental

A Mach Zehnder interferometer consisting of two kinds of waveguides with a width of 4μm is designed and prepared. The first is an evanescent coupler with two parallel waveguides of 400μm long (see figure 6.9). The distance between these waveguides is 2μm to ensure the splitting of the light at the input and recombining it at the output of the Mach Zehnder. The second is a bent waveguide with radius of curvature varying from 6mm to 10mm. For this study the waveguides are etched down to 1.4μm to ensure a better confinement than the 1.8μm etched straight waveguides. A small core and a silicon oxide isolation layer is chosen to prevent the losses in the waveguide. The process flow to prepare a Mach Zehnder interferometer is given in appendix B.9.

![Figure 6.9: A Mach Zehnder interferometer (a) cross-section and (b) top-view.](image)
Waveguide propagation loss measurements were carried out at 633nm for the transverse electric (TE) and transverse magnetic (TM) polarizations. The polarization dependent losses (PDL) is the loss difference between the TE and TM polarization (TM-TE). The light of a He-Ne Laser is collimated and focused onto the waveguide input using lenses. The spot size of the beam at the working distance is $3\mu m$. A polarization controller, placed between the light source and the lenses, is used to adjust the light polarisation for both TE and TM-guided mode excitation. Once the losses versus propagation lengths graph are plotted and the origin is found, the scattering loss can be subtracted easily. Moreover, this origin yields information about Fresnel losses and the mode mismatch between the incoming beam and the small size waveguides.

Results and discussions

Figure 6.10 shows the waveguide losses of the $4\mu m$ wide waveguides for TE and TM polarization. The losses do not exceed $4\text{dB/cm}$ and the PDL are less than $0.7\text{dB/cm}$. For devices requiring few millimeter of propagation such as modulators and attenuators, the on-chip losses are negligible.

![Graph showing PDL loss of 4μm wide waveguides](image)

Figure 6.10: The PDL loss of the $4\mu m$ wide waveguides.

Figure 6.11 shows the bending losses measured at 633nm. These losses are the difference between measured loss and material loss. One can observe that a radius of 6mm and higher do not generate losses. Furthermore, simulations performed with a 2D bend mode solver show that bend losses stay below $0.5\text{dB/90°}$ even for a $2\text{mm}$ radius (in that case the confinement of the waveguide is increased etching down to $1\mu m$).

A Mach Zehnder interferometer with an $8\text{mm}$ bend radius and $1.5\text{cm}$ length has shown an on-chip loss of $5\text{dB}$ and a PDL of $0.2\text{dB}$. A $2\text{mm}$ bend radius
Figure 6.11: The bending losses measured at 633nm.

Figure 6.12: The loss as a function of the thermal annealing temperature.

will reduce the size down to 0.5cm, bringing the on-chip loss down to 1dB.

The propagation loss as a function of thermal annealing temperature is presented in figure 6.12. The zero birefringence condition is found for an annealing temperature of 500°C. Moreover, the propagation losses are improved, moving down to 2dB/cm.

In short the preliminary results indicate that PECVD SiC films with a high refractive index enable the integration of Mach Zehnder interferometers and electronics in silicon.

6.3.2 Humidity sensor

Measurement and control of humidity are necessary, for example in the meteorological service, food processing, air conditioning, horticulture and electronics
processing. Several traditional materials such as polymer, ceramics, porous Si have been used as the sensing element of a humidity sensor successfully [132].

In this section, we present porous SiC - a new sensing material fully compatible with standard Si processing. The main advantage of porous SiC over previous materials that can also be integrated into standard Si processing, is that porous SiC can withstand harsh environments and is not very sensitive to temperature fluctuations.

**Experimental**

Porous SiC films are prepared by electrochemical anodizing PECVD SiC films in various HF solutions (including Triton X100 surfactant). Anodized current densities $J_A$ are in the range of 1-50mA/cm$^2$. Anodization times $t_A$ are in between 30 seconds and 10 minutes. A porous SiC humidity sensor is prepared as follows (see detailed in appendix B.10). First, a SiC film is deposited on the front side of a Si substrate. A thin layer of Al is evaporated on the backside to make the electrode. Porous SiC is made in an HF solution. Then a porous Au is sputtered on the top of the porous SiC film. Figure 6.13 shows the structure of a porous SiC humidity sensor.

![Cross section of a tested humidity sensor](image)

Figure 6.13: A cross section of a tested humidity sensor.

In order to examine the usability of a porous SiC humidity sensor in harsh environments, it is placed in two test conditions, one at 85%RH and 85°C for 24 hours and the other at the outlet of a car exhaust while driving around for about 30 minutes. The characteristics of the sensor are measured immediately afterwards. Both measurements are performed at 25°C and 35°C to investigate the effect of increased temperature on the sensor. An HP 4194A impedance/gain phase analyzer meter operated at frequencies between 100Hz-100kHz is used for capacitance measurements. The results are normalized to the capacitance value for 10%RH to show the relative response.
Results and discussions

Figure 6.14 shows the sensitive response in the range of 10-90%RH of a porous SiC humidity sensor before and after burn-in up to 55°C. After burn-in, the response is about 80% in sensitivity. The burn-in period improved the device stability as well as reducing the hysteresis effect. The sensitivity of porous SiC humidity sensor depends on the porous making conditions (i.e., the HF concentration).

![Graph showing the sensitive response of a porous SiC sensor before and after burn-in.](image)

Figure 6.14: The humidity sensitive response of a porous SiC sensor.

Figure 6.15: The humidity sensitive response of a porous SiC sensor after being in 85%RH and 85°C for 24 hours.

Figure 6.15 shows a response of a porous SiC humidity sensor after being in 85%RH and 85°C for 24 hours. There is not much hysteresis or saturation at high RH values. After placed in, the response has decreased to an overall
Figure 6.16: The humidity sensitive of a porous SiC sensor measured at 25°C and 35°C after being exposed to a car exhaust for 30 minutes.

sensitivity of 55%; and there seems to be an increase in the hysterisis.

For the second test, the response is measured at 25°C followed by increasing the test chamber to 35°C. The responses are shown in figure 6.16.

It can be concluded that PECVD SiC is a suitable material to make porous formation for humidity sensors. Although the sensitivity of a porous SiC humidity sensor is not as high as other types of sensors, it shows stable characteristic after treating in two harsh environments.

6.4 Concluding remarks

We have manufactured several devices using PECVD SiC films. These devices show the possibility of integrating SiC-based sensors and actuators with on-chip electronics, offering components highly suited for operation in harsh environments.

Our all-dry post-processing surface micromachining module has proven its feasibility to realize electrostatic actuated switches, pressure sensors and vertical accelerometers - all compatible with conventional IC processes and then allowing integration with on-chip electronics.

Another application of a PECVD SiC film with a high refractive index has been investigated in a Mach Zehnder interferometer. In addition, a porous SiC material prepared by electrochemical anodization of PECVD SiC films has demonstrated attractive characteristics for use as a sensing element in humidity sensors.
Chapter 7

Conclusions and future work

7.1 Conclusions

The SiC material deposited by PECVD techniques is an excellent candidate for a structural layer in post-processing surface micromachining, since the deposition and patterning processes are carried out at low temperature (< 400°C). Furthermore, its inertia in many corrosive media is attractive for application in harsh environments. In this thesis, we have studied the properties of a PECVD SiC film for post-processing surface micromachining for sensors and actuators that can be integrated with on-chip electronics.

SiC films deposited by a PECVD technique are amorphous (a-SiC). The most important physical constants of these films, such as stress, strain, Young’s modulus, bandgap, and dielectric constant have been measured. The mechanical, optical and electrical properties of the films depend strongly on their chemical composition, which is related to the deposition parameters, doping and post-deposition annealing treatment.

The Taguchi method provides a systematic approach for studying PECVD SiC films. The influence of the deposition parameters, including temperature, pressure, gas flow rate and power, on the properties of PECVD SiC films has been mapped out. Among the main parameters, the SiH₄ gas flow rate of the PECVD process was found to play a crucial role in controlling the properties of SiC films. This investigation also allowed the selection of the most suitable deposition conditions to obtain layers with desired characteristics for a specific application.

By combining the Taguchi method with a least-squares technique, an empirical model to control the PECVD process has been obtained. This empirical model takes into account the interaction between parameters and allowed us
to select their proper values to prepare a low tensile stress SiC film as required for surface micromachined devices.

In examining the effect of in-situ doping on structural properties of an a-SiC film, it can be assumed that when P atoms are added, they replace C positions in the bonds between C and Si, while B atoms replace Si positions. Based on FTIR analysis, the Si-C bond in an undoped film is stronger than in a p-type film, while it is weaker than in n-type films. A model based on their electronegativity has been proposed to explain this effect of in-situ doping.

Lowering the sheet resistance of an a-SiC film is a difficult problem, for which the laser annealing technique offers a possible solution. The results indicate that this technique is beneficial for p-type a-SiC films as the resistance can be reduced from $10^{10}\Omega/\square$ to $10^{3}\Omega/\square$. The structure re-ordering in a PECVD SiC film from an amorphous to a nano-polycrystalline state has been observed after post-deposition laser annealing.

A number of materials have been considered as sacrificial layers when using PECVD a SiC film as a structural layer. In particular, we have proposed an all-dry post-processing surface micromachining module using a PECVD SiC film as a structural layer and polyimide as a sacrificial layer. This module has demonstrated the ability to prevent stiction by realizing a free-standing microstructure.

These PECVD SiC films have attracted quite some interests from the design coming. Several devices have been realized utilizing one or another specific characteristic of these films. For example, the low stress SiC films have been applied for micromechanical components such as electrostatic switches, pressure sensors and vertical accelerometers. Applications of PECVD SiC films that benefit from other attractive properties such as a high refractive index (waveguides, interferometers) and the possibility to make porous layers (humidity/gas sensors) have further demonstrated the potential of the PECVD SiC layers and their compatibility with on-chip electronics.

### 7.2 Future work

This thesis has studied SiC material for post-processing surface micromachining. The material is prepared by the PECVD technique at low temperature and therefore fully compatible with conventional IC processing. For certain other applications, further investigation on the effect of this technique for other properties of a-SiC films might be required.

More investigations should be performed to understand the properties of laser annealed SiC films with low resistivity and their new applications. There
should be more experiments must be done to study the thermal properties of PECVD SiC, which have not done in this thesis yet. These properties are important for stress investigation of material.

So far, the field of nanotechnology is becoming mature with nanomaterials playing an increasingly important role in microsystem applications. Amidst various materials of nanosize, carbon nanotubes (CNTs) have received special interest in MEMS/NEMS research.

Future integration with conventional microelectronics as well as development of novel devices requires that CNTs can be grown in highly ordered arrays or located at a specially defined position. One approach is to grow CNTs on a nanosize pores anodic aluminium oxide (AAO) template on Si substrate using methane in an RF PECVD at 400°C without using a catalyst transition metal has started performing in DIMES.

The low-temperature IC-compatible process above is very attractive as it allows integration of CNT devices with on-chip electronics. In a more general setting, we expect the integration of nanosize devices with on-chip electronics as an important future research direction for the cost-sensitive production of microsystems, sensors, actuators and electronics with a higher or optimized performance compared to conventional materials.
Appendix A

The Taguchi method

A.1 The Taguchi table

Table A.1 shows the orthogonal array for designing the experiments (column 2) and the calculated constants of mechanical, optical and electrical properties of PECVD SiC films (column 3).

The values are the deposition rate (DR), etch rate (ER), stress (σ), dielectric constant (ε), refractive indices at 0nm and 633nm (n633 and n0), dispersion energy (E_d), oscillation energy (E_o) and carrier to mass ratio (N/m).

A.2 ANOVA

Analysis of Variance (ANOVA) is used to evaluate the effect of deposition parameters on properties of PECVD SiC films.

Preparation of the supplementary table

Calculate level totals for each factor, which is assigned to a column of an orthogonal array (see table A.1) to obtain table A.2.

Calculation of total variation and variation of factors

The total variation $S_T$ can be calculated as follows

$$S_T = \sum y_i^2 - \frac{\sum y_i^2}{27}$$

(A.1)
<table>
<thead>
<tr>
<th>Run</th>
<th>Input</th>
<th>Output</th>
<th>( \frac{N}{m} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
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<td>28.76</td>
<td>83.40</td>
</tr>
<tr>
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<td>43.73</td>
<td>85.50</td>
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<td>81.20</td>
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<td>31.28</td>
<td>83.50</td>
</tr>
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<td>2 3 1 2 2</td>
<td>51.64</td>
<td>75.20</td>
</tr>
<tr>
<td>18</td>
<td>2 3 1 2 3</td>
<td>61.23</td>
<td>72.30</td>
</tr>
<tr>
<td>19</td>
<td>3 1 3 2 1</td>
<td>63.97</td>
<td>101.0</td>
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<tr>
<td>20</td>
<td>3 1 3 2 2</td>
<td>70.26</td>
<td>85.20</td>
</tr>
<tr>
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<td>3 1 3 2 3</td>
<td>75.19</td>
<td>26.00</td>
</tr>
<tr>
<td>22</td>
<td>3 2 2 1 1</td>
<td>28.38</td>
<td>76.00</td>
</tr>
<tr>
<td>23</td>
<td>3 2 2 1 2</td>
<td>43.73</td>
<td>65.50</td>
</tr>
<tr>
<td>24</td>
<td>3 2 2 1 3</td>
<td>51.00</td>
<td>71.00</td>
</tr>
<tr>
<td>25</td>
<td>3 3 1 3 1</td>
<td>59.11</td>
<td>98.60</td>
</tr>
<tr>
<td>26</td>
<td>3 3 1 3 2</td>
<td>74.53</td>
<td>87.70</td>
</tr>
<tr>
<td>27</td>
<td>3 3 1 3 3</td>
<td>87.46</td>
<td>83.00</td>
</tr>
</tbody>
</table>
Table A.2: The supplementary table

<table>
<thead>
<tr>
<th>Factor</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>A₁</td>
<td>( y₁ + y₂ + y₃ + y₄ + y₅ + y₆ + y₇ + y₈ + y₉ )</td>
</tr>
<tr>
<td>A₂</td>
<td>( y₁₀ + y₁₁ + y₁₂ + y₁₃ + y₁₄ + y₁₅ + y₁₆ + y₁₇ + y₁₈ )</td>
</tr>
<tr>
<td>A₃</td>
<td>( y₁₉ + y₂₀ + y₂₁ + y₂₂ + y₂₃ + y₂₄ + y₂₅ + y₂₆ + y₂₇ )</td>
</tr>
<tr>
<td>B₁</td>
<td>( y₁ + y₂ + y₃ + y₁₀ + y₁₁ + y₁₂ + y₁₉ + y₂₀ + y₂₁ )</td>
</tr>
<tr>
<td>B₂</td>
<td>( y₄ + y₅ + y₆ + y₁₃ + y₁₄ + y₁₅ + y₂₂ + y₂₃ + y₂₄ )</td>
</tr>
<tr>
<td>B₃</td>
<td>( y₇ + y₈ + y₉ + y₁₆ + y₁₇ + y₁₈ + y₂₅ + y₂₆ + y₂₇ )</td>
</tr>
<tr>
<td>C₁</td>
<td>( y₁ + y₂ + y₃ + y₁₁ + y₁₂ + y₁₉ + y₂₀ + y₂₁ + y₂₄ )</td>
</tr>
<tr>
<td>C₂</td>
<td>( y₄ + y₅ + y₆ + y₁₀ + y₁₁ + y₁₂ + y₂₅ + y₂₆ + y₂₇ )</td>
</tr>
<tr>
<td>C₃</td>
<td>( y₇ + y₈ + y₉ + y₁₃ + y₁₄ + y₁₅ + y₁₉ + y₂₀ + y₂₁ )</td>
</tr>
<tr>
<td>D₁</td>
<td>( y₁ + y₂ + y₃ + y₁₃ + y₁₄ + y₁₅ + y₂₅ + y₂₆ + y₂₇ )</td>
</tr>
<tr>
<td>D₂</td>
<td>( y₄ + y₅ + y₆ + y₁₆ + y₁₇ + y₁₈ + y₁₉ + y₂₀ + y₂₁ )</td>
</tr>
<tr>
<td>D₃</td>
<td>( y₇ + y₈ + y₉ + y₁₀ + y₁₁ + y₁₂ + y₂₂ + y₂₃ + y₂₄ )</td>
</tr>
<tr>
<td>E₁</td>
<td>( y₁ + y₄ + y₇ + y₁₀ + y₁₃ + y₁₆ + y₁₉ + y₂₂ + y₂₅ )</td>
</tr>
<tr>
<td>E₂</td>
<td>( y₂ + y₅ + y₈ + y₁₁ + y₁₄ + y₁₇ + y₂₀ + y₂₃ + y₂₆ )</td>
</tr>
<tr>
<td>E₃</td>
<td>( y₃ + y₆ + y₉ + y₁₀ + y₁₂ + y₁₅ + y₁₈ + y₂₁ + y₂₄ + y₂₇ )</td>
</tr>
<tr>
<td>Total</td>
<td>( \sum y_i )</td>
</tr>
</tbody>
</table>

The total amount of deviation is called the general mean \( S_m \)

\[
S_m = \sum \frac{y_i^2}{27} \tag{A.2}
\]

The variation \( S_X \) due to a factor \( X \) can be calculated as follows

\[
S_X = \frac{(X₁² + X₂² + X₃²)}{3} - S_m \tag{A.3}
\]

Let \( f_X \) be the degree of freedom of the factor \( X \). The variance per unit degree of freedom \( V_X \) for the factor \( X \) is

\[
V_X = \frac{S_X}{f_X} \tag{A.4}
\]

The degree of contribution \( \rho_X \) of the factor \( X \) is calculated by

\[
\rho_X = \frac{S_X}{S_T} \times 100\% \tag{A.5}
\]
Table A.3: ANOVA table for deposition rate (DR) characteristics.

<table>
<thead>
<tr>
<th>Factors</th>
<th>f</th>
<th>S</th>
<th>V</th>
<th>ρ(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2</td>
<td>3034</td>
<td>1517</td>
<td>10.90</td>
</tr>
<tr>
<td>B</td>
<td>2</td>
<td>3220</td>
<td>1610</td>
<td>11.57</td>
</tr>
<tr>
<td>C</td>
<td>2</td>
<td>10607</td>
<td>5304</td>
<td>38.12</td>
</tr>
<tr>
<td>D</td>
<td>2</td>
<td>119</td>
<td>59</td>
<td>0.42</td>
</tr>
<tr>
<td>E</td>
<td>2</td>
<td>2915</td>
<td>1457</td>
<td>10.47</td>
</tr>
<tr>
<td>(e)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>28.52</td>
</tr>
<tr>
<td>T</td>
<td>10</td>
<td>27824</td>
<td>-</td>
<td>100.00</td>
</tr>
</tbody>
</table>

Table A.4: ANOVA table for etch rate (ER) characteristics.

<table>
<thead>
<tr>
<th>Factors</th>
<th>f</th>
<th>S</th>
<th>V</th>
<th>ρ(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2</td>
<td>2819</td>
<td>1410</td>
<td>23.72</td>
</tr>
<tr>
<td>B</td>
<td>2</td>
<td>1543</td>
<td>771</td>
<td>12.98</td>
</tr>
<tr>
<td>C</td>
<td>2</td>
<td>2724</td>
<td>1362</td>
<td>22.92</td>
</tr>
<tr>
<td>D</td>
<td>2</td>
<td>741</td>
<td>307</td>
<td>6.32</td>
</tr>
<tr>
<td>E</td>
<td>2</td>
<td>728</td>
<td>364</td>
<td>6.12</td>
</tr>
<tr>
<td>(e)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>27.94</td>
</tr>
<tr>
<td>T</td>
<td>10</td>
<td>11885</td>
<td>-</td>
<td>100.00</td>
</tr>
</tbody>
</table>

With an ANOVA table, it is easy to observe and compare variances and degrees of contribution of the deposition parameters on properties of SiC thin films.

ANOVA tables
Table A.5: ANOVA table for stress ($\sigma$) characteristics.

<table>
<thead>
<tr>
<th>Factors</th>
<th>f</th>
<th>S</th>
<th>V</th>
<th>$\rho$(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2</td>
<td>115622</td>
<td>57811</td>
<td>9.76</td>
</tr>
<tr>
<td>B</td>
<td>2</td>
<td>335481</td>
<td>167740</td>
<td>28.31</td>
</tr>
<tr>
<td>C</td>
<td>2</td>
<td>479617</td>
<td>239808</td>
<td>40.47</td>
</tr>
<tr>
<td>D</td>
<td>2</td>
<td>6602</td>
<td>301</td>
<td>0.56</td>
</tr>
<tr>
<td>E</td>
<td>2</td>
<td>187473</td>
<td>93737</td>
<td>15.82</td>
</tr>
<tr>
<td>(e)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>5.08</td>
</tr>
<tr>
<td>T</td>
<td>10</td>
<td>1185242</td>
<td>-</td>
<td>100.00</td>
</tr>
</tbody>
</table>

Table A.6: ANOVA table for bandgap ($E_g$).

<table>
<thead>
<tr>
<th>Factors</th>
<th>f</th>
<th>S</th>
<th>V</th>
<th>$\rho$(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2</td>
<td>0.2</td>
<td>0.1</td>
<td>15.26</td>
</tr>
<tr>
<td>B</td>
<td>2</td>
<td>0.04</td>
<td>0.02</td>
<td>2.82</td>
</tr>
<tr>
<td>C</td>
<td>2</td>
<td>0.86</td>
<td>0.43</td>
<td>57.33</td>
</tr>
<tr>
<td>D</td>
<td>2</td>
<td>0.04</td>
<td>0.02</td>
<td>2.82</td>
</tr>
<tr>
<td>E</td>
<td>2</td>
<td>0.03</td>
<td>0.01</td>
<td>1.93</td>
</tr>
<tr>
<td>(e)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>19.84</td>
</tr>
<tr>
<td>T</td>
<td>10</td>
<td>1.5</td>
<td>-</td>
<td>100.00</td>
</tr>
</tbody>
</table>

Table A.7: ANOVA table for absorption energy ($E_{04}$).

<table>
<thead>
<tr>
<th>Factors</th>
<th>f</th>
<th>S</th>
<th>V</th>
<th>$\rho$(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2</td>
<td>0.03</td>
<td>0.02</td>
<td>5.03</td>
</tr>
<tr>
<td>B</td>
<td>2</td>
<td>0.01</td>
<td>0.01</td>
<td>2.09</td>
</tr>
<tr>
<td>C</td>
<td>2</td>
<td>0.42</td>
<td>0.21</td>
<td>62.33</td>
</tr>
<tr>
<td>D</td>
<td>2</td>
<td>0.02</td>
<td>0.01</td>
<td>2.85</td>
</tr>
<tr>
<td>E</td>
<td>2</td>
<td>0.02</td>
<td>0.01</td>
<td>2.43</td>
</tr>
<tr>
<td>(e)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>25.27</td>
</tr>
<tr>
<td>T</td>
<td>10</td>
<td>0.68</td>
<td>-</td>
<td>100.00</td>
</tr>
</tbody>
</table>
Table A.8: ANOVA table for dielectric constant ($\varepsilon$).

<table>
<thead>
<tr>
<th>Factors</th>
<th>f</th>
<th>S</th>
<th>V</th>
<th>$\rho(%)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2</td>
<td>12.51</td>
<td>6.25</td>
<td>20.68</td>
</tr>
<tr>
<td>B</td>
<td>2</td>
<td>3.92</td>
<td>1.96</td>
<td>6.48</td>
</tr>
<tr>
<td>C</td>
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<td>42.14</td>
<td>21.07</td>
<td>69.69</td>
</tr>
<tr>
<td>D</td>
<td>2</td>
<td>1.53</td>
<td>0.76</td>
<td>2.52</td>
</tr>
<tr>
<td>E</td>
<td>2</td>
<td>0.1</td>
<td>0.05</td>
<td>0.16</td>
</tr>
<tr>
<td>(e)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.47</td>
</tr>
<tr>
<td>T</td>
<td>10</td>
<td>60.47</td>
<td>-</td>
<td>100.00</td>
</tr>
</tbody>
</table>

Table A.9: ANOVA table for refractive index ($n_{633}$).

<table>
<thead>
<tr>
<th>Factors</th>
<th>f</th>
<th>S</th>
<th>V</th>
<th>$\rho(%)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2</td>
<td>0.3</td>
<td>0.15</td>
<td>17.32</td>
</tr>
<tr>
<td>B</td>
<td>2</td>
<td>0.1</td>
<td>0.05</td>
<td>5.60</td>
</tr>
<tr>
<td>C</td>
<td>2</td>
<td>1.24</td>
<td>0.62</td>
<td>72.40</td>
</tr>
<tr>
<td>D</td>
<td>2</td>
<td>0.05</td>
<td>0.02</td>
<td>2.73</td>
</tr>
<tr>
<td>E</td>
<td>2</td>
<td>0.01</td>
<td>0.003</td>
<td>0.39</td>
</tr>
<tr>
<td>(e)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.56</td>
</tr>
<tr>
<td>T</td>
<td>7</td>
<td>10</td>
<td>1.71</td>
<td>100.00</td>
</tr>
</tbody>
</table>

Table A.10: ANOVA table for refractive index ($n_0$).

<table>
<thead>
<tr>
<th>Factors</th>
<th>f</th>
<th>S</th>
<th>V</th>
<th>$\rho(%)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2</td>
<td>0.25</td>
<td>0.12</td>
<td>25.46</td>
</tr>
<tr>
<td>B</td>
<td>2</td>
<td>0.07</td>
<td>0.03</td>
<td>7.00</td>
</tr>
<tr>
<td>C</td>
<td>2</td>
<td>0.61</td>
<td>0.3</td>
<td>62.85</td>
</tr>
<tr>
<td>D</td>
<td>2</td>
<td>0.03</td>
<td>0.02</td>
<td>3.31</td>
</tr>
<tr>
<td>E</td>
<td>2</td>
<td>0.003</td>
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<td>0.31</td>
</tr>
<tr>
<td>(e)</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.07</td>
</tr>
<tr>
<td>T</td>
<td>10</td>
<td>0.96</td>
<td>-</td>
<td>100.00</td>
</tr>
</tbody>
</table>
Table A.11: ANOVA table for dispersion energy ($E_d$).

<table>
<thead>
<tr>
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<th>$f$</th>
<th>$S$</th>
<th>$V$</th>
<th>$\rho(%)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2</td>
<td>115</td>
<td>58</td>
<td>55.79</td>
</tr>
<tr>
<td>B</td>
<td>2</td>
<td>28</td>
<td>14</td>
<td>13.56</td>
</tr>
<tr>
<td>C</td>
<td>2</td>
<td>16</td>
<td>8</td>
<td>7.89</td>
</tr>
<tr>
<td>D</td>
<td>2</td>
<td>12</td>
<td>6</td>
<td>5.89</td>
</tr>
<tr>
<td>E</td>
<td>2</td>
<td>16</td>
<td>8</td>
<td>7.71</td>
</tr>
<tr>
<td>(e)</td>
<td></td>
<td></td>
<td></td>
<td>9.16</td>
</tr>
<tr>
<td>T</td>
<td>10</td>
<td>206.23</td>
<td>-</td>
<td>100.00</td>
</tr>
</tbody>
</table>

Table A.12: ANOVA table for oscillator energy ($E_o$).

<table>
<thead>
<tr>
<th>Factors</th>
<th>$f$</th>
<th>$S$</th>
<th>$V$</th>
<th>$\rho(%)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2</td>
<td>0.05</td>
<td>0.02</td>
<td>0.38</td>
</tr>
<tr>
<td>B</td>
<td>2</td>
<td>0.03</td>
<td>0.01</td>
<td>0.22</td>
</tr>
<tr>
<td>C</td>
<td>2</td>
<td>11.39</td>
<td>5.69</td>
<td>92.73</td>
</tr>
<tr>
<td>D</td>
<td>2</td>
<td>0.05</td>
<td>0.02</td>
<td>0.38</td>
</tr>
<tr>
<td>E</td>
<td>2</td>
<td>0.34</td>
<td>0.17</td>
<td>2.73</td>
</tr>
<tr>
<td>(e)</td>
<td></td>
<td></td>
<td></td>
<td>3.56</td>
</tr>
<tr>
<td>T</td>
<td>10</td>
<td>12.28</td>
<td>-</td>
<td>100.00</td>
</tr>
</tbody>
</table>

Table A.13: ANOVA table for carrier to mass ratio ($\frac{N}{m^*}$).

<table>
<thead>
<tr>
<th>Factors</th>
<th>$f$</th>
<th>$S$</th>
<th>$V$</th>
<th>$\rho(%)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>2</td>
<td>276</td>
<td>138</td>
<td>14.25</td>
</tr>
<tr>
<td>B</td>
<td>2</td>
<td>195</td>
<td>97</td>
<td>10.04</td>
</tr>
<tr>
<td>C</td>
<td>2</td>
<td>1143</td>
<td>571</td>
<td>58.97</td>
</tr>
<tr>
<td>D</td>
<td>2</td>
<td>78</td>
<td>39</td>
<td>4.01</td>
</tr>
<tr>
<td>E</td>
<td>2</td>
<td>89</td>
<td>45</td>
<td>4.59</td>
</tr>
<tr>
<td>(e)</td>
<td></td>
<td></td>
<td></td>
<td>8.14</td>
</tr>
<tr>
<td>T</td>
<td>10</td>
<td>1938</td>
<td>-</td>
<td>100.00</td>
</tr>
</tbody>
</table>
Appendix B

Process flow for test structures and devices

B.1 van der Pauw structure preparation

Using mask set DI815 (PS/PC/IC)

1. Substrate: Si wafer <100>, thickness of 500μm, resistivity of 7-21Ωcm.

2. Making an alignment mask

   (a) Thermal oxidation: Oxide thickness is 500±30nm.

   (b) Mask definition (mask COMURK): coat 1.4μm of photoresist AZ3012 and bake at 95°C in 1 minute on Convac module 2000, exposure with energy of 120mJ on ASML PAS 5000/50, bake at 115°C in 1 minute, develop with developer Shipley MF322, bake at 100°C in 1 minute on Convac module 2000 (Program A).

   (c) SiO wet etching: in H₂O/TRITON X-100 in 1 minute and BHF 1:7 in 10 minutes, rinse in demiwater in 5 minutes and drying.

   (d) Hydrophobic test.

   (e) Cleaning: remove photoresist in aceton 1 minute, HNO₃ 100% in 10 minutes, demiwater in 5 minutes, HNO₃ 65% at 105°C in 10 minutes, demiwater in 5 minutes and dry (non-metal procedure).

   (f) Wet oxidation: Total oxide thickness is 750±20nm.

3. Depositing a 500nm PECVD SiC film in an Novellus Concept One.
4. Mask definition (mask PS): coat 2μm of photoresist AZ3017 and bake at 95°C in 1 minute on Convac module 2000, exposure with energy of 120mJ on ASML 5000/50, bake at 115°C in 1 minute, develop with developer Shipley MF322, bake at 100°C in 1 minute on Convac module 2000 (Program B)

5. SiC plasma etching: in an Alcatel GIR300 system using gases CF₄:SF₆:O₂ = 70:10:10, power of 60W, pressure of 500mbar (recipe standard).


7. Depositing a 700nm PECVD SiO film in an Novellus Concept One.

8. Mask definition (mask PC): follow program A.

9. SiO wet etching: see step 2c.

10. Cleaning: remove photoresist in aceton in 1 minute and follow nonmetal procedure.

11. Sputtering a 1.4μm Al film in a Trikon system.

12. Mask definition (mask IC): follow program B.

13. Al plasma etching: in Trikon Omega 201 using gas: HBr:Cl₂=40:30, pressure of 5mTorr, power of 500W (IPC)and 35W (bias) at 25°C. (Recipe A114-350)

14. Cleaning: strip photoresist in O₂ plasma, HNO₃ 100% in 10 minutes, demiwater in 5 minutes and dry (metal procedure).

15. Alloy at 400-450°C in H₂/N₂ in Tempress system.

**B.2 MIM structure preparation**

Using mask set DI715 (IC/CT/CAP/IN)

1. Substrate: Si wafer <100>, thickness of 500μm, resistivity of 7-21Ωcm.


3. Sputtering a 0.6μm Al film in a Trikon system.

4. Mask definition (mask IC): follow program B.
5. Al plasma etching: in Trikon Omega 201 using gas: HBr:Cl₂=40:30, pressure of 5mTorr, power of 500W (IPC) and 50W (bias) at 25°C. (Al06-350 recipe).

6. Cleaning: strip photoresist in O₂ plasma, and follow metal procedure.

7. Deposit 1μm PECVD SiO in Novellus Concept One.

8. Mask definition (mask CT): follow program B.

9. Oxide plasma etching: in DRYTEK Triode 384T using gases C₂F₆:CHF₃ = 36:144, pressure of 180mTorr, power of 300W (RIE mode) at 12°C. (Recipe standard)

10. Cleaning: strip photoresist in O₂ plasma and follow metal procedure.

11. Depositing a 500nm PECVD SiC film in Novellus Concept One.

12. Mask definition (mask CAP): follow program B.


15. Sputtering a 1.4μm Al film in Trikon system.

16. Mask definition (Mask IN): follow program B.


18. Cleaning: strip photoresist in O₂ plasma, and follow metal procedure.

B.3 MIS structure preparation

1. Substrate: Si wafer <100>, thickness: 500μm, resistivity of 7-21Ωcm.

2. Cleaning: follow nonmetal procedure.

3. Native oxide removal: in 0.55% HF/IPA in 4 minutes, rinse in demiwater in 5 minutes and dry.

4. Depositing a PECVD SiC film in Novellus Concept One.

5. Backside oxide etching: 0.55% HF in 2 minutes, rinse in demiwater in 5 minutes and dry.
6. Sputtering a 0.4µm Al film on backside and 0.6µm Al film on frontside in Trikon system.

7. Mask definition (mask MINOX-PS): follow program B.


B.4 Polyimide preparation

1. Substrate: Si wafer <100>, thickness: 500µm, resistivity of 7-21Ωcm.

2. Spinning adhesion promoter VM651 0.01%, spin speed: 5000rpm, bake at 100-150°C in 60 seconds on hot plate.

3. Spinning polyimide PI2610: spin wafer at 500 rpm for 5 seconds, ramp to maximum spin speed (2000rpm to 5000rpm); Prebake at 90°C in about 3 minutes and at 180°C for 90 seconds on hot plate.

4. Curing polyimide: load wafers at 150°C in N₂, ramp to 400°C at a rate of 5°C/min., curing for 30 minutes at 400°C.

5. Cleaning: in 65% HNO₃ at 105°C, demiwater in 5 minutes and dry (polyimide procedure).

B.5 All-dry post-processing

Mask set EI996 (SAC/PS1)

1. Substrate: Si wafer <100>, thickness of 500µm, resistivity of 7-21Ωcm.

2. Making an alignment mask

   (a) Mask definition (mask COMURK): follow program A.

   (b) Si plasma etching: in Trikon Omega 201 using gases Cl₂:HBr=80:40, pressure of 60mTorr, power of 500W (ICP) and 20W (bias) at 20°C.

3. Cleaning: strip photoresist in O₂ plasma and follow non-metal procedure.

5. Depositing a 300nm PECVD SiO in Novellus Concept One.

6. Mask definition (mask SAC): follow program A.

7. SiO plasma etching: in Alcatel GIR300 system using standard recipe.


9. Removing the SiO film in HF 1% in 2 minutes, rinse in demiwater in 5 minutes and dry.


11. Depositing a 500nm PECVD SiC film in Novellus Concept One.

12. Mask definition (mask PS1): Program B.

13. SiC plasma etching: in Alcatel GIR300 system using standard recipe.

14. Etching polyimide in O₂ plasma in 15 minutes in Tepla stripper.

B.6 Switch preparation

Mask set EI996 (SAC/PS1/IC)

1. Substrate: Si wafer <100>, thickness of 500μm, resistivity of 7-21Ωcm.


3. Cleaning: strip photoresist in O₂ plasma and follow non-metal procedure.


5. Polyimide patterning: see appendix B.5. steps 3-9.


7. Depositing a 800nm PECVD SiC film in Novellus Concept One.

8. Mask definition (mask PS1): follow program B.


11. Sputtering a 1.4\(\mu\)m Al film in Trikon system.
12. Mask definition (mask IC): follow program B.

B.7 Pressure sensor preparation

1. Substrate: Si wafer <100>, thickness of 500\(\mu\)m, resistivity of 7-21\(\Omega\)cm.
3. Cleaning: strip photoresist in O\(_2\) plasma and follow non-metal procedure.
4. Sputtering a 0.6\(\mu\)m Al film in Trikon system.
5. Mask definition (mask IC): follow program A.
11. Depositing a 800nm PECVD SiC film in Novellus Concept One.
12. Sputtering a 1.4\(\mu\)m Al film in Trikon system.
13. Mask definition (mask PS1): follow program B.
15. Cleaning: follow metal procedure.
16. Depositing a 500nm PECVD SiC film in Novellus Concept One.
17. Window opening: follow program B.
18. SiC plasma etching: in Alcatel GIR300 system using standard recipe.
19. Etching polyimide in Tepla stripper.
20. Depositing a 500nm PECVD SiC film in Novellus Concept One.
B.8 Accelerometer preparation

1. Substrate: Si wafer <100>, thickness of 500\(\mu\)m, resistivity of 7-21\(\Omega\)cm.


3. Cleaning: strip photoresist in O\(_2\) plasma and follow non-metal procedure.

4. Sputtering a 0.6\(\mu\)m Al film in Trikon system.

5. Mask definition (mask IC): follow program A.


8. Depositing 1\(\mu\)m PECVD PSG in Novellus Concept One.

9. Mask definition (mask SAC): follow program B.

10. PSG plasma etching: in Drytek Triode 384T using standard recipe.


12. Depositing a 1\(\mu\)m PECVD SiC film in Novellus Concept One.

13. Sputtering an 800nm Al film in Trikon system.

14. Mask definition (mask PS1): follow program B.

15. Al and SiC plasma etching: in Trikon \(\Omega\)mega 201 using recipe Al14-350.


17. Removing PSG in HF 73%. Freeze drying.

B.9 Mach Zehnder interferometer

1. Substrate: Si wafer <100>, thickness of 500\(\mu\)m, resistivity of 7-21\(\Omega\)cm.

2. Depositing a 1\(\mu\)m PECVD SiO film and a 2\(\mu\)m PECVD SiC film in Novellus Concept One.
3. Mask definition (mask EI1138): coat 2 $\mu$m of photoresist AZ3017 and bake at 95°C in 1 minute on CONVAC module 2000, exposure with energy of 120mJ on EV 420, bake at 115°C in 1 minute, develop with developer MF322, bake at 100°C in 1 minute on CONVAC module 2000.

4. SiC plasma etching: in Alcatel GIR300 system using standard recipe.

5. Cleaning: strip photoresist in O$_2$ plasma and follow non-metal procedure.

### B.10 Humidity sensor preparation

1. Substrate: Si wafer $<100>$, thickness of 500$\mu$m, resistivity of 7-21$\Omega$cm.

2. Depositing a 1$\mu$m PECVD SiC film in Novellus Concept One.

3. Al evaporation backside.

4. Making porous SiC: anodization in HF 73%.


Bibliography


Summary

Title: PECVD Silicon Carbide - a Structural Material for Surface Micromachined Devices

By: Hoa Thi Mai PHAM

Integrating surface micromachining into standard processing can complicate the process, reduce yield, and thus increase cost. It is therefore important to establish a strategy in terms of how and when the surface micromachined devices can be inserted into a standard IC process. Post-processing surface micromachining is a flexible and economically attractive approach to overcome the above mentioned problems.

In post-processing surface micromachining the temperature must be maintained below 400°C as dictated by the presence of aluminum metallization used in most conventional IC processes. It is therefore necessary to develop micromachining processes that either use existing layers or additional layers that can be deposited and patterned at temperature lower than 400°C. Materials prepared by PECVD techniques, as well as metals and polyimides have got attentions for this purpose. For each material considered there are two important aspects to take into account: the compatibility with IC processes and the specific properties of this material.

Moreover, in designing microfabricated devices, it is important to be aware that the properties of thin film materials are often significantly different from their bulk form. Much of this disparity arises from the difference in the processes used to produce thin film materials and bulk materials. Many microstructures have revealed that properties of a thin film material can vary tremendously from film to film without a careful process control. Any high precision and high reliability application requires that significant effort be directed toward quantifying precisely the material properties of the films being employed.
In this work, we investigate the properties of SiC thin films prepared by PECVD technique and its applicability for post-processing surface micromachining to integrate sensors and actuators with on-chip electronics. The PECVD SiC material is an excellent candidate for a structural layer in post-processing surface micromachining, since deposition and patterning processes are carried out at low temperature (< 400°C). Furthermore, its inertia in many corrosive media is attractive for application in harsh environments.

Due to the large number of parameters involved, a design of experiment is necessary. The Taguchi method provides a systematic approach for studying PECVD SiC films. The influence of the deposition parameters, including temperature, pressure, gas flow rate and power, on the properties of PECVD SiC films has been mapped out. Among the main parameters, the SiH₄ gas flow rate of the PECVD process plays a crucial role in controlling the properties of SiC films. This investigation also allows the selection of the most suitable deposition conditions to obtain layers with desired characteristics for a specific application. Further, by combining the Taguchi method with a least square technique, an empirical model to control the PECVD process has been obtained. This empirical model taking into account the interaction between parameters allows us to select their proper values to prepare a low tensile SiC film as required for surface micromachined devices.

In examining the effect of in-situ doping on structural properties of an a-SiC film, it can be assumed that when P atoms are added, they replace C positions in the bonding between C and Si while B atoms replace Si positions. Based on FTIR analysis, the Si-C bond in an undoped film is stronger than in a p-type film, while it is weaker than in an n-type film. A model based on electronegativities of atoms has been proposed to explain this effect.

SiC films deposited by a PECVD technique are in an amorphous state (a-SiC). The most important physical constants of these films, such as stress, strain, bandgap, and dielectric constant have been calculated. The mechanical, optical and electrical properties of the films depend strongly on the chemical composition, which is related to the deposition parameters, doping and post-deposition annealing treatment.

Lowering the sheet resistance of an a-SiC film is a difficult problem, for which the laser annealing technique offers a possible solution. The results indicate that this technique is beneficial for a p-type a-SiC films as the resistance can be reduced from 10¹⁰Ω/□ to 10³Ω/□. The structure re-ordering in a PECVD SiC film from an amorphous to a nano-polycrystalline state has been observed after a post-deposition laser annealing.

A number of materials have been considered as sacrificial layers when using
PECVD a SiC film as a structural layer. Especially, we have proposed an all-dry post-processing surface micromachining module using a PECVD SiC film as a structural layer and polyimide as a sacrificial layer. This module has demonstrated the ability for stiction prevention in realizing the free-standing microstructures.

These PECVD SiC films have attracted quite some interests from the design coming. Several devices have been realized utilizing one or another specific characteristic of these films. For example, the low stress SiC films have been applied for micromechanical components such as electrostatic switches, pressure sensors and vertical accelerometers. Applications of PECVD SiC films that benefit from other attractive properties such as a high refractive index (waveguides, interferometers) and the possibility to make porous layers (humidity/gas sensors) have further demonstrated the potential of the PECVD SiC layers and their compatibility with on-chip electronics.
Samenvatting*

Titel: PECVD Silicium Carbide - een Structureel Materiaal voor Surface Micromachined Componenten.

Door: Hoa Thi Mai PHAM

Integratie van surface micromachining in een standaard IC proces kan het proces ingewikkelder maken, de opbrengst doen dalen en derhalve de kosten doen stijgen. Het is hierom belangrijk om een strategie te bepalen inzake de manier en het moment waarop de surface micromachined componenten kunnen worden geïmplementeerd in een standaard IC proces. Een economisch aantrekkelijke en flexibele benadering is die van de zogenaamde post-proces surface micromachining technologie.

In de post-proces surface micromachining technologie dient de temperatuur beneden de 400°C te blijven vanwege de aanwezigheid van aluminium metallisatie, welke wordt gebruikt in de meeste conventionele IC processen. Het is daarom noodzakelijk om micromachining processen te ontwikkelen die, of gebruik maken van bestaande lagen, of van extra lagen die bij een temperatuur lager dan 400°C kunnen worden gedeponeerd en gedefinieerd. Om deze redenen hebben materialen gemaakt met behulp van PECVD techniek alswel metalen en polyimiden de aandacht. Er zijn twee belangrijke aspecten waarmee rekening moet worden gehouden bij de keuze van het te gebruiken materiaal: de compabilititeit met IC processen en de specifieke eigenschappen van het materiaal.

Bij het ontwerpen van microgefabriceerde componenten, is het bovendien belangrijk om zich bewust te zijn van de significante verschillen in eigenschappen tussen dunne film materiaal en bulk materiaal. Deze ontstaan veelal door

*Summary in Dutch
de verschillen in de produktie processen onderling. Menige microstructuren hebben aangetoond dat, zonder een zorgvuldige proces controle, de eigenschappen van een dunne film materiaal sterk kunnen variëren van film tot film. Elke hoge precisie, hoge betrouwbaarheid IC toepassing vereist dat significante inspanning wordt gefocuseerd op het nauwkeurig quantificeren van de materiaaleigenschappen.

In dit werk onderzoeken we de eigenschappen van dunne film SiC bereid met behulp van PECVD techniek en haar toepasbaarheid voor post-proces surface micromachining met als doel om sensoren en actuatoren te integreren met on-chip elektronica. Het PECVD SiC materiaal is een uitstekende kandidaat als structurele film voor de post-proces surface micromachining techniek, aangezien de depositie en de patroondefinitie worden uitgevoerd bij een lage temperatuur (< 400°C). Bovendien is het, vanwege zijn inertie in vele corrosieve media, attractief voor toepassingen in agressieve milieus.

Vanwege het grote aantal depositie parameters is een “design of experiments” noodzakelijk. De Taguchi methode verschaf een systematische benadering voor het bestuderen van PECVD SiC films. De invloed van de depositie parameters zoals temperatuur, druk, gas inlaat snelheid en vermogen op de eigenschappen van de PECVD SiC films zijn in kaart gebracht. De silaan gas inlaat snelheid in het PECVD proces speelt een cruciale rol in de beheersing van de eigenschappen van de SiC films.

Dit onderzoek geeft eveneens een procedure voor het bepalen van de meest geschikte geschikte depositie condities om materiaal met de gewenste karakteristieken voor een specifieke toepassing te verkrijgen. Vervolgens is door het combineren van de Taguchi methode met de kleinste kwadraat methode een empirisch model verkregen om het PECVD proces te sturen. Met dit empirisch model waarin de interactie tussen parameters wordt meegerekend, kunnen we de juiste waarden selecteren om een low-tensile-stress SiC film te maken zoals benodigd voor de surface micromachined structuren.

Door bestudering van het effect van in-situ dotering op de mechanische eigenschappen van een a-SiC film, kan worden afgeleid dat wanneer P atomen worden toegevoegd, deze de C posities innemen van de C-Si verbinding terwijl B atomen de Si posities innemen. Gebaseerd op FTIR analyse resultaten is bepaald dat de Si-C binding sterker is in een ongedoteerde film dan in een p-gedoteerde film, terwijl deze zwakker is in een n-gedoteerde film. Om dit effect te verklaren is een model, gebaseerd op electronegativiteit van atomen, voorgelegd.

SiC films gedeponeerd met behulp van de PECVD techniek zijn amorf. De belangrijkste fysische constanten van deze films, zoals stress, strain, bandgap
en dielektrische constante zijn bepaald. De mechanische, optische en elektrische eigenschappen van de films hangen sterk af van de chemische samenstelling, welke weer wordt gerelateerd aan de depositie parameters, de dotering en post-depositie anneal behandeling.

Het verlagen van de sheet weerstand van een a-SiC film is een lastig probleem, waarvoor de laser anneal techniek een mogelijke oplossing biedt. De resultaten tonen aan dat deze techniek nuttig is voor p-gedoteerd a-SiC lagen waarbij de weerstand kan worden verlaagd van $10^{10}\Omega/\square$ naar $10^{3}\Omega/\square$. Na de post-depositie laser anneal werd meestal een herordering van de structuur, van een amorfe naar een nano-polykristallijne toestand, in de PECVD SiC film waargenomen.

Een aantal verschillende materialen zijn toegepast als sacrificial laag voor het gebruik bij de structurele PECVD a-SiC laag. In het bijzonder hebben we een volledig droog post-proces surface micromachining module voorgesteld waarin een PECVD SiC film als structurele laag wordt toegepast en polyimide als sacrificieel laag. Deze module heeft zijn capaciteit aangetoond door “stiction” te voorkomen bij de realisatie van vrijstaande microstructuren.

Deze PECVD SiC filmlagen hebben aanzienlijke aandacht verkregen bij het ontwerpen van nieuwe devices. Meerdere devices zijn al gerealiseerd waarbij gebruik is gemaakt van een bepaalde, specifieke karakteristiek van deze films. Bijvoorbeeld, de SiC films met lage stress, zijn gebruikt in micromechanische componenten zoals elektrostatische schakelaars, druk sensoren en vertikale versnellingsmeters. Toepassingen van PECVD SiC films die voordeel halen uit andere aantrekkelijke eigenschappen zoals een hoge brekingsindex (golfgeleiders, interferometers) en de mogelijkheid om poreuze lagen te maken (vochtigheid/gas sensoren) hebben verder het potentieel bewezen van deze films en hun compatibiliteit met on-chip elektronica.
Publications

Journal publications


Conference publications


7. E.J.Connolly, G.M.O’Halloran, H.T.M. Pham, P.M.Sarro and P.J.French, “Investigation of the influence of measurement frequency on the response of humidity sensors based on porous silicon, porous polysilicon


Acknowledgements

Here I won't bore you with any further technical details. I must say that this work was truly a labor of love. Although the process was difficult, it feels very rewarding to have completed a thesis. Of course, this is easy to say now that the thesis is finished and I have some time to reflect on the experience and prepare for graduation. Looking back, I simply cannot believe that I have written this book. I am so proud of the work that I am going to spend all my time showing it off to my friends and others.

I know, however, that I would not have been able to finish this thesis without the help and support of a number of people whom I want to thank here.

First of all, I would like to deeply thank my promoter Professor Lina Sarro. With her enthusiasm, her inspiration, and her great efforts to explain things clearly and simply, she has helped to make this work fun for me. Throughout my work, she provided encouragement, sound advice, good teaching, good company, and lots of good ideas. I would have been lost without her. I would like to thank Professor Kees Beenakker for granting me a PhD position in the Electronic Components, Technology and Materials Laboratory. I still remember how nervous I was when I had to answer so many difficult questions during our first meeting in Vietnam. I am grateful to Professor Paddy French for many fruitful suggestions and discussions in this thesis. I appreciate all his funny ideas in every meeting we had. Many thanks go to Professor Achim Burghartz, Professor Lis Nanver, and Bert Goudena for their effort to provide me a pleasant research environment.

I thank members of my doctoral committee for taking time out of their busy schedules to review this thesis, providing insightful suggestions and commentary on the manuscript.

I acknowledge the Technology Foundation STW (project DMF.5103) for supporting this work. I want to thank members of the STW user committee for their interest in my work and for their advice.

Much appreciation is due to Lukasz Pakula, Eamon Connolly, and Gregory
Pandraud for their excellent contributions to my work. I also want to thank Alvise Bagolini and Tolgay Akkaya for being such nice students under my supervision. I really enjoyed working with all of them in such an international group (Polish, Irish, Italian, Vietnamese, French and Dutch).

I would like to thank all members of the ECTM group who gave me an enjoyable environment to explore my passions and whom I will be forever grateful to have worked with:

Wim van der Vlist who showed his patience to teach me since the first lesson on working in the cleanroom. Tom Scholtes who always took care of my safety in the laboratory and somehow always found my mistakes. Mario Laros who gave me many good suggestions on plasma etching and helped me to solve many problems, but waiting for him five minutes to get into the cleanroom seemed to never end. Cassan Visser who helped me a lot with SORA measurement. John Slabbeokorn for his experience in lithography and laser annealing. Ruud Klerks and Alfred Apon for their skill in keeping the equipment working very well. Jan Groeneweg for preparing a lot of chemical solutions for me. Hugo Schellevis and Alex van den Bogaard in the PAC committee for many tough discussions, allowing me to work with many "untraditional" things in the cleanroom. Loek Steenweg, Henk van Zeijl, Wim Wien, Lorentz Ramsay, Jurgen Bertens, Carl Agatz and Peter Kroon for their kind assistance. My special thanks go to Charles de Boer. I know how lucky I was to be his friend. Everything he has done for me these last four years is unforgettable. Of course, I must thank him for the very hard work of translating the summary of this book into Dutch.

I would like to thank Dr. Wim Sloof and Kees Kwakernaak in the Department of Materials Science and Engineering for performing EPMA measurement, Dr. Romeo Bernini at the Institute for Electromagnetic Sensing of the Environment - CNR, Italy for the FTIR results, Mark Zuiddam for the AFM images, and Tjander Nathoen for helping with many electrical measurements.

I would like to thank all the non-academic staff for their constant cooperation during my stay here. I am grateful to the secretaries for assisting me in many different ways. Marysia Langendijk and Marian Roozenburg deserve special mention. I want to thank Mrs. Mirjam J. Nieman for correcting my English in this thesis.

I would like to take this opportunity to thank the Board of Directors at the Institute of Materials Science (IMS), the Vietnamese Academy of Science and Technology (VAST), all my colleagues at the Electronic Materials Division, and staff members too for their help and support during my absence.

My life in Holland was never boring because of international friends whose
personality always impressed me. I have learnt much from them about many aspects of life. I would like to thank all my roommates, all PhD students and postdocs in Electronic Components, Technology and Materials and Electronic Instrument Laboratories for the relaxed atmosphere and the many conversations, of which at least a few were scientific. I would like to thank all members of our badminton club (Silvana Milosavljevic, Ellen Neihof, Arjen Klaver, Vikas Rana, Jan Groeneweg, Charles de Boer, Bert Goudena) for keeping me healthy. I will never forget the many secret tactics and political plays we had for winning every Tuesday.

I would like to thank all my friends, who always listened whenever I complained about my life. It would be a big omission to forget to express my appreciation to all e-mail from them everyday. They kept me thinking I would never be alone. I must give my special thanks to Son, who makes me laugh and never let me feel low. I thank him and his family for their caring for years. I am sure all my friends in Amsterdam will never forget many parties and gaming overnights with “De Kolonisten van Catan”, and being too exhausted to do anything the day after (not too healthy but a lot of fun). I am grateful to Viet and Nga for their friendship. Of course, I should mention their daughter, Minh Anh, who has always been my favourite little girlie since she was born. I adore every moment she gives me her love in her own way.

I am happy having my family (my brother, my sister-in-law, and my sister) around. My brother deserves my appreciation for always looking after me. His effort to improve my English has made this book easier to understand. Lastly, and most importantly, I wish to thank my parents. Without their constant support and love, I would not be the person I am today, and I would not be able to appreciate the simple things in life. Mummy and Daddy, to you I dedicate this thesis.
Biography

Hoa T.M. Pham was born in Hanoi, Vietnam in 1974. She received the Bachelor of Science Degree in Chemistry with specialization in Chemistry of Natural Compounds, from Hanoi University, Vietnam in 1994. In 1996, she received the Master of Science Degree in Materials Science from the International Training Institute for Materials Science in Vietnam. In September 1996, she became a researcher in the Institute of Materials Science, Vietnamese Academy for Science and Technology. At that time, her work focused on research and development of new porous materials for chemical sensors.

In September 2000, she joined the Electronic Component, Technology and Materials Laboratory of the Delft University of Technology, Delft, the Netherlands, as a PhD student with Professor P.M. Sarro, working on materials for post-processing surface micromachining for sensors and actuators. She was responsible for the investigation of properties of materials and development processes to apply materials for sensors and actuators. During this time, she was a supervisor of Masters students at Delft University of Technology. From September 2004, her interest focuses on the project “Nanostructure formation using nanotemplate for MEMS/NEMS devices”.

In December 2004, she will return to Vietnam to rejoin the Institute of Materials Science, Vietnamese Academy for Science and Technology. Her research interests include electronic material processing and MEMS/NEMS technology.