Micromachining Based On Porous Silicon

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This thesis is presented for the degree of Doctor of Philosophy from The University of Western Australia

2016
Abstract

Micromachining based on fabrication of multilayer structures on top of a silicon wafer or other substrate has extensively leveraged modern integrated circuit techniques, blending mechanical and electrical applications. This capability renders the building of microelectromechanical systems (MEMS) for a diverse range of products including automobile airbag systems, display systems, inkjet cartridges, new generation sensors and optical devices. With the rapid development of micromachining, researchers are driven to find materials which are compatible with existing processes and have enhanced properties that can extend the capabilities of MEMS devices. Porous silicon (PS), which possesses the properties of room temperature photoluminescence, large surface area and easily tuneable refractive index, is one of the most promising materials to explore in the fabrication of next generation MEMS devices.

Various microstructures including light emitting diodes, sensors and optical filters have been built using PS. However, PS based microstructures are either limited in performance due to non-uniform porosity, low achievable aspect ratio and weak scalability (large size of the structure), or are difficult to fabricate with complementary metal–oxide–semiconductor (CMOS) compatible techniques. Therefore, comprehensive CMOS compatible PS micromachining processes for fabricating scalable, complex and uniform porosity PS-MEMS structures are required. This would enable PS to functionalise as a structural layer in MEMS and be incorporated in modern electronic industry.

In this work, detailed investigations have been carried out into micromachining processes that will facilitate scalable, complex and uniform porosity PS-MEMS. Comprehensive PS surface micromachining processes were developed, including: PS
formation, N₂ annealing, photolithography, inductively coupled plasma reactive-ion etching (ICP-RIE), repeated photolithography, electropolishing and critical point drying. A novel pore filling technique employing spin-on glass (SOG) was developed to enable, for the first time, thick (defined as >1 µm) meso-PS films to be processed using standard photolithographic techniques, enabling high quality patterning with conventional photoresist on PS. Electropolishing using the same experimental apparatus as the PS anodisation (in which PS is created from silicon wafers) was utilised to release PS microstructures from the silicon substrate. This technique was simple to implement and achieved uniform etching of the silicon surface under the PS microstructures. Undercut of electropolishing with different masking layers were studied, subsequently a photoresist masking layer with adhesion enhancement was employed in the electropolishing process, which effectively limited the etching undercut.

After implementing the newly developed processes into PS-MEMS fabrication, well defined all-PS microstructures with laterally uniform porosity were successfully released. A PS grating with a thickness of 2 µm and aspect ratio of ~1:1 was successfully fabricated with the novel pore filling technique and standard photolithography process. The processes enable PS to work as the structural layer in scalable, complex and laterally uniform porosity MEMS devices. The lack of a separate release (sacrificial) layer for the MEMS device and the use PS for the structural layer and silicon as the support wafer (handle) allows the creation of a truly all-silicon MEMS device.

The final matter to be addressed in this work was that of vertically uniform porosity, and with it, substantial investigations into film stress. As key factors to understand the performance of PS-MEMS structures, residual stress and stress gradient in PS films were investigated, and corresponding stress tuning methods were studied.

Both X-ray diffraction (XRD) rocking curve and radius of curvature based methods were employed to study the residual stress in PS films. It was found that porosity variation achieved by changing the anodisation current density during fabrication can be
a simple way of tuning the film stress. Ambient oxidation of as-fabricated and low temperature (300 °C) annealed PS can produce compressively stressed films, a tendency which increases with time exposed to air. The effect of low temperature annealing can be reversed by a short HF dip, which provides a path to adjust the stress in the PS film. The effects of hydrogen desorption, oxidation and nitridation, modified via annealing temperature ($T$) and ambient, were studied through analysis of PS physical properties and the mechanism of stress evolution. It was found that at temperatures above 500 °C, the nitridation prevents oxidation effects on stress. The effect of annealing was significantly reversed by a short HF dip, except in the case of nitridised samples annealed above 550 °C. Annealing duration and flow rate showed different effects on stress, providing other options in stress control. The repeated annealing results of PS samples indicate that the PS film experienced a permanent structural change after 600 °C annealing, resulting in a level of stress that was subsequently fixed in the sample.

Stress gradients in PS films were also investigated and mitigated through a porosity compensation technique, in which the current conditions were adjusted during the PS formation process. While current control has previously been used to alter film properties such as refractive index, it has never before been used to compensate for stress. Subsequently, methods for tuning the film stress and stress gradient were developed.

The stress gradient tuning was applied along with the previously established micromachining processes to achieve high quality released PS MEMS structures. Subsequently a high resonant frequency of released PS microbeam fabricated with the established processes was measured, which was used for estimating both the residual stress and Young’s modulus of the released PS microstructures. By monitoring the change in the resonance of PS microstructures over time, a potential mechanism for sensing applications utilising these released PS microstructures was also demonstrated. Sensing of vapours was successfully carried out with released cantilevers and doubly clamped microbeams, demonstrating the possibility to utilise microstructures fabricated with the novel multistep PS-MEMS processes to work as chemical sensors.
Combining the established PS micromachining processes, optimised film stress, stress gradient control methods and monitoring of the resonant frequency measurement, will enable PS to be considered as a viable platform for ultra-sensitive MEMS sensors. Such sensors can leverage the very large surface area of the films to enhance chemical detection, create laminated layers to achieve specific optical or thermal properties, or utilise structures with large gaps between the structural and substrate layers to minimise effects such as squeezed film damping. As such a diverse new generation PS-MEMS devices are one step closer to realisation as the original results of this work.
Acknowledgements

I would like to start by acknowledging my coordinating supervisor Prof Adrian Keating, who has been always extremely supportive and patient for my project, even since the first day I contacted him for PhD candidature application. Adrian has provided numerous suggestions and brilliant ideas in problem solving, programming and technical support issues, which were the critical motivations for me to complete this project. I would also like to acknowledge my co-supervisor Prof Giacinta Parish, who has provided enormous valuable discussions and observations, even the guidance and help in improving my writing skills and data presentation techniques. I would sincerely thank both my supervisors, not only for their significant contribution in helping me get through my thesis, but for their concern on my daily life as well.

I would like to thank all the other senior members in Microelectronics Research Group, including Winthrop Prof Lorenzo Faraone, Prof Mariusz Martyniuk, Prof Dilusha Silva, Associate Prof Gilberto Umana-Membreno, Associate Prof Jarek Antoszewski, Associate Prof Wen Lei, Associate Prof Gino Putrino, Associate Prof Yongling Ren, Associate Prof Martin Hill, Dr Roger Jeffery, Ms Sabine Betts, Ms Karen Kader and Mr George Voyt, who have provided valuable advice and help through my PhD study. Many thanks to Associate Prof Andrew Johnson in the CMCA for the help on the XRD measurements.

I would also like to thank Dr Meifang Lai for helping me through my early experimentation stage, and N. Radha Krishnan for the help on RTA recipes programming. To my fellow students, Haifeng Mao, Farah Muhammad Khir, Roozbeh Anvari, Dhirendra Tripathi, Ben Cheah, Fei Guo, Michal Zawierta, Won Jae Lee,
Imitiaz Madni, Amit Choudhary, Hemendra Kala, Anna Podolska, Jorge Silva Castillo, Jega Gurusamy and Baishen Wei, you made my PhD life full of laughter and happiness.

I would like to thank my parents, who have been very supportive to my decision and study, though quitting a good job and studying as a PhD student in another country were not what they expected. I would like to express my specific appreciation to my wife, Bin Chen, who has scarified a lot and provided enormous support during the last four years. In addition, thank her for bringing the wonderful gift, our daughter Anya, to us.

I would like to thank the University of Western Australia for providing the precious opportunity and the scholarships for me to undertake my PhD programme.
Statement of Originality

The work contained in this thesis is, to the best of the author's knowledge, original and contains no material previously published by another person except where due references are made. The material in this thesis has not been previously submitted, in part or in full, for a degree at this or any other higher education institution.
Author list of publications


**Xiao Sun**, Giacinta Parish, Adrian Keating, “Released Porous Silicon Microbeams for Static and Dynamic Mode Sensing”, in preparation.
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CHAPTER 1
INTRODUCTION

An overview of porous silicon (PS) and its applications is presented, especially with the application of micromachining to PS. Current obstacles to PS based microelectromechanical systems (PS-MEMS) fabrication processes are discussed in detail. Subsequently the specific goals and outline of this thesis are presented.

1.1 POROUS SILICON BASED MICROMACHINING

Porous silicon (PS) is a unique material which exhibits a range of interesting properties including large surface area (up to 1000 m$^2$/g [1, 2]), photoluminescence [3] and easily tuneable porosity which determines the density, Young’s modulus [4] and refractive index [5] of the film. All these characteristics render it a promising material in scalable, complex microelectromechanical systems (MEMS) fabrication which leverages processes from the integrated circuit industry. Therefore, as the key to enable PS as a structural layer in MEMS fabrication, established PS micromachining processes are in great demand.

Porous silicon, formed via the partial electrochemical dissolution of crystalline silicon (Si) in HF/Ethanol solution, was original discovered by Uhlir at Bell Labs [6] in 1956 when investigating electrochemical methods of cleaning the surfaces of germanium and silicon ingots. Subsequently the detailed fabrication process of PS film was investigated by Turner [7] in 1958 from the same group. In the years since, PS has gained significant attention due to its biocompatibility [8], photoluminescence [9] and large surface area [10].
PS has been exploited in various areas including light emitting diodes [11], sensors [12, 13], optical detectors [13, 14], reflectors [15-17], filters [18-20] and waveguides [21, 22]. Many PS applications have utilised the large surface area or tuneable refractive index of the film by incorporating these characteristics as a functional part of the device.

With the large surface area and porous internal structure, PS based sensors can provide significant sensitivities with the ability to detect target analytes, such as the capture of biological molecules [23] or adsorption of gas/liquid [24], at very small detection limits. The tuneable refractive index makes PS a suitable platform for fabricating optical structures with controllable reflectance or transmittance [15-20].

The use of PS as a support material for MEMS devices provides an opportunity for it to have even greater impact, but requires further investigation and integration with electronic industrial processes. PS was widely used as a sacrificial layer in micromachining process [25, 26] for decades. As understanding of the porous layer formation and characterisation has improved, PS has started to be considered and used as an active component of MEMS devices [27, 28].

The advancement of PS based microelectromechanical systems (PS-MEMS) fabrication techniques enables PS to be utilised in conventional MEMS processes and work as key sensing or optical component in devices. Complex PS-MEMS structures have been fabricated utilising micromachining processes. As an example, the scanning electron microscopy (SEM) image of an optical filter as a result of utilising PS-MEMS processes is shown in Figure 1.1 [29]. The PS optical filter was actuated by thermal heating from an applied voltage. While impressive, the MEMS device leveraged, rather than addressed, the limitations of PS, namely the non-uniform porosity and tendency to oxidise, in order to release thick, oxidised porous silicon based devices.
Figure 1.1 SEM image of a tuneable optical interference filter fabricated from oxidised PS (image taken from [29]).

1.2 CURRENT OBSTACLES IN PS-MEMS

A comparison of different technologies in scale of size is shown in Figure 1.2 [30]. The length scale for MEMS structures is typically from 100 nm to 1 mm, which renders the effects of many parameters different from macrosystems in ordinary life.

Figure 1.2 Comparison of different technologies in scale of size (image adapted from [30]).
The effects of length scale ($L$) on natural frequency ($f_n$) and various inertial forces are shown in Figure 1.3(a)-(c). Compared to that for macrosystems, a significant increase of the natural frequency is achieved in the MEMS region, as shown in Figure 1.3(a). Furthermore, as shown in Figure 1.3(b)-(c), when the length scale is reduced to be in the MEMS region, the surface tension and electrostatic forces become dominant in the microstructures, compared to gravity and inertial forces which are dominant in macrosystems.

Figure 1.3 Scaling effects of different parameters: (a) relationship between length scale and natural frequency; (b) relationship between length scale and gravity, surface tension; (c) relationship between length scale and inertial force, electrostatic force.
However, previous PS-MEMS structures have been large (on the order of 1×1 mm²) or poorly defined (significant under-mask etching and non-uniform porosity) [31, 32]. This negates a significant advantage of MEMS, which is that their small size provides both robustness against inertial effects and high resonance. Consider for example high sensitivity biosensors based on MEMS cantilevers [33-35] as illustrated in Figure 1.4(a). This type of sensor operates via two main read-out methods, namely static mode (typically detection of the height change) and dynamic mode (typically detection of motion/resonance). In the static mode illustrated in Figure 1.4(b), the deflection of the microbeam is measured using optical readout techniques which are able to achieve extremely high precision sensitivity. Such a technique relies on stress changes to induce deflection and not inertial (gravitational) effect. Inertia effects are considered negligible in such beams due to their small size as illustrated in Figure 1.3(b)-(c). Such sensors based on PS-MEMS are investigated and discussed in Section 6.4.1. In contrast, the dynamic mode illustrated in Figure 1.4(c) senses the change in the resonant frequency of the beam due to analytes that become attached (adsorbed or absorbed).

\[ f_0 \]

\[ f_0 \downarrow \]

**Figure 1.4** Example of high sensitivity biosensor based on MEMS cantilever. (a) The cantilever has been functionalised, but no detection event has yet occurred, (b) static mode detection, the protein has bonded to the functionalisation layer, and the resulting surface stress causes the cantilever to deform, (c) dynamic mode detection, the protein has bonded to the functionalisation layer, and the resulting mass change causes resonant frequency change of the cantilever. Image adapted from [36].
In the dynamic mode of operating, the resonant frequency of a cantilever is given by:

$$f_0 = \frac{1}{2\pi} \sqrt{\frac{k}{m}} = \frac{1}{2\pi} \sqrt{\frac{Ewt^3}{4mL^3}} \quad \text{Equation 1-1}$$

where \(m\) is the mass of the cantilever beam, \(E\) is the Young’s modulus of the beam material, and \(w\), \(t\), and \(L\) are respectively the cantilever width, thickness and length. Looking deeper, it can be observed that the change in frequency due to a mass change can be determined by differentiating Equation 1-1 to give:

$$\frac{\partial f_0}{\partial m} = \frac{1}{2\pi} \left( -\frac{1}{2m} \right) \sqrt{\frac{k}{m}} = -\frac{f_0}{2m} = S_m \quad \text{Equation 1-2}$$

where \(S_m\) is the sensitivity of the measurement to a mass change. Again small size resulting is a small mass is important for high performance MEMS sensors based on dynamic mode sensing, as a high resonant frequency which arises due to a small mass (as observed from Equation 1-1) is essential for high sensitivity (high \(S_m\)) biosensors [33-35].

Comparing a beam made from a bulk material such as Si to a beam made from PS, it will be shown later that the sensitivity \(S_m\) is independent of porosity. Hence at first glance it may appear that the PS based microcantilever would have little advantage over its bulk counterpart. However this type of measurement is actually limited by the smallest frequency \(\partial f_0\) which can be detected so that the product of \(\partial m \cdot S_m\) is important. Sensitivity analysis in microcantilevers made from bulk materials considers only \(S_m\) as the available detection (surface) area depends only on the geometry and not the material used. This is not the case for PS as the large surface area provides an opportunity for very large mass change (\(\partial m\)).

In Figure 1.5(a) a simple model for the increase of surface area of a PS as a function of porosity is considered. In this model the surface area is calculated assuming a simple spherical area (pore) removed from a unit cell of Si. In Figure 1.5(b), the ratio of the surface area of a PS cantilever relative to the surface area of a bulk Si cantilever (dimensions 100 \(\mu\text{m}\times20 \mu\text{m}\times2.5 \mu\text{m}\)) is shown for various pore size diameters of
interest to this work. At high porosities of around 80%, the surface area ranges from 160 to 960 times that of bulk Si. It is the very large surface area of these films to allow a significant change in $\partial m \cdot S_m$ to occur, leading to significant changes in the resonant frequency that is measured. This provides a huge opportunity for increased detection sensitivity from microcantilever biosensors made from PS.

![Figure 1.5](image)

**Figure 1.5 Surface area investigation of PS:** (a) simple model of surface area increase of PS, (b) the ratio of the surface area of a PS cantilever relative to the surface area of a bulk Si cantilever, cantilever size of 100 $\mu$m×20 $\mu$m×2.5 $\mu$m. Data adapted from [37].

Measurement of the frequency from sensors utilising dynamic mode readout can be performed optically or electrically (capacitive sensing), allowing the readout method to address multiple microstructures simultaneously, which is cost effective [36]. This sensing method provides a path to production of large sensor arrays, allowing scalable sensing in a range of applications. Given its importance, dynamic mode optical measurements of the resonant frequency will be demonstrated for released PS microbeam in Section 6.3.

By understanding how the unique properties of MEMS sensors can be enhanced by utilising porous silicon, a motivation for developing micromachining and characterisation of PS microstructures emerges. To address the challenges to achieve such a goal, an approach to fabricate small size, scalable and complex PS-MEMS structures will be discussed in detail in the following sections.
1.2.1 PS micromachining processes

Semiconductor materials such as silicon (Si), germanium (Ge) and SiN have been extensively studied and applied in MEMS. However, very few PS-MEMS devices have been investigated or commercially used. The most significant reason for this is the difficulty in modifying PS films to be compatible with modern metal–oxide–semiconductor (CMOS) and integrated circuit industries with a scalable PS-MEMS fabrication process. Though carbonisation and nitridation techniques that passivate the surface offer the best opportunity to bridge the gap with integrated circuit fabrication [38, 39], no comprehensive techniques to render mesoporous silicon a robust, passivated material which could be used as the structural layer in MEMS device fabrication has been developed. Mesoporous silicon is considered particularly important due to its nanometer pore size, providing not only large surface area but allowing low optical losses in the infrared [40].

Techniques for combining PS with standard micromachining processes to build complex microstructures would enable a significant range of applications, with biosensors already discussed being only one. However, previously reported PS-MEMS devices such as gas sensors [41], biological sensors [32] and optical filters [29, 31, 42] were mainly fabricated through a predefined patterning process utilising a mask or patterned layer on Si prior to anodisation (post-CMOS process). Typically such techniques use mask assisted etching based on a robust mask such as a metal layer (usually Au or Pt) [43, 44] or thick photoresist layer [41] which is deposited and patterned on the silicon surface. Subsequent anodisation is carried out by immersing the sample in HF based electrolyte. As such, the requirement is that the masking layer should be robust enough to withstand etching of HF.

As typical and widely applied structures in surface micromachining, microstructures can be released through a series of processes based on N$_2$ annealed PS, which will be detailed in Section 5.2. An illustration of such a released PS cantilever is shown in Figure 1.6. In such a structure, if the film has non-uniform lateral porosity, film properties including Young’s modulus, residual stress and refractive index will be significantly affected, resulting in non-uniform rigidity, optical efficiency and structural quality. As a result, non-uniform porosity in the structural layer can lead to deformation
or failure of the device. Therefore, it is critical to fabricate PS microstructures with uniform porosity for the applications and the processes to be investigated in this work.

A schematic view of the processing steps involved with post-CMOS techniques is illustrated in Figure 1.7 [41], largely based on using a thick photoresist layer. The as-fabricated circuit including the required sensor electronics is shown in Figure 1.7(a), where an oxide passivation layer is used in the well which will ultimately contain the PS sensor. After the thick photoresist masking layer was defined on the top surface of the chip (Figure 1.7(b)), and subsequent removal of oxide passivation layer (Figure 1.7(c)), a selective formation of PS region (Figure 1.7(d)) was carried out.

Due to the isotropic etching by HF during the anodisation process, this post-processing technique results in very low lateral uniformity of porosity in the PS film, as well as undesirable under-mask etching. This is shown in Figure 1.8 and corresponds to the step shown in Figure 1.7(d). The non-uniform porosity and under-mask etching can significantly affect the performance of the device when using PS as a structural layer.
Figure 1.7 Schematic view of an example of processing steps for post-patterning anodisation using a thick photoresist layer (image taken from [41]): (a) section of the chip for PS formation; (b) thick photoresist mask definition for both passivation removal and selective PS formation; (c) after passivation removal; (d) after electrochemical etching for PS formation and subsequent photoresist mask removal.
Post-PS patterning (not the post-CMOS patterning just discussed), is designed to create patterns in the PS film(s) after a layer or multilayers of PS have been formed on top of a Si substrate. Post-PS processing techniques have previously been demonstrated without masks [46] or by a stamping technique through dry-soft lithography on PS [47, 48]. Unfortunately, both such post-PS patterning methods result in low resolution structures with non-uniform porosity, and are not considered CMOS compatible.

For PS-MEMS, a uniform porosity and a well defined PS microstructure with controlled stress and stress gradient are required to create a high quality structural MEMS platform. Furthermore, the process must be compatible with a high volume (scalable) manufacturing process. Lai et al. demonstrated a process based on N$_2$ annealing which passivated the surface, reducing oxidation in ambient air, and providing a path to make...
the films compatible with standard photolithography [49]. This previous approach makes PS a suitable platform for creating patterned structures of laterally uniform porosity, and allows multistep processing through repeated anodisation, annealing and photolithography to be performed. The key to the approach by Lai et al. was a robust SiOxNy film which passivated the PS film stabilising it against chemical and environmental attack [45]. However, no thick PS (>1 µm) structure has been successfully fabricated due to the limitation of the material previously used to fill the pores of PS during the photolithographic process (which will be detailed discussed in Section 2.3.2).

For many surface micromachined applications, multilayer films up to 5 µm need to be considered. For example, when considering suspended microbeams, from which many MEMS devices are formed, the rigidity is defined as:

$$EI_z = E \frac{bt^3}{12}$$  \hspace{1cm} \text{Equation 1-3}

where $E$ is the Young’s modulus of the microbeam, $I_z$ is the moment of inertia in the microbeam bending direction $z$, $b$ and $t$ are the width and thickness of the microbeam. Rigidity is a key parameters when determining parameters such as effective spring constant ($k$), and the larger the rigidity, the larger the stiffness of the beam. Stiffer beams ($k$) result is higher resonant frequency according to Equation 1-1, which is important to achieving high sensitivity MEMS based biosensors. Equation 1-3 indicates that the $EI_z$ increases with $t^3$ (in the direction of $z$), so a thickness $t$ going for example from 1 µm to 2.5 µm increases the rigidity by a factor of 15, resulting in significantly decreased curvature/deflection and increased stiffness of the microbeam. Furthermore, without the ability to form thicker layers, optical multi-layer films cannot be developed, somewhat limiting the scope of these PS-MEMS devices. For example, a distributed Bragg reflector (DBR) operating a wavelength of $\lambda=1.55$ µm, requires a quarter-wave layer thickness of $d=258$ nm assuming a refractive index of $n=1.5$. Hence, a 10-layer distributed Bragg reflector (DBR) would require around 2.5 µm.

Therefore, the current range of processing techniques limits the design freedom and impedes multistep PS-MEMS fabrication processes which are required to implement surface micromachining of PS films. Since repeated patterning and CMOS compatible
processes are critical for fabricating scalable, complex structures [41], current limitations on PS-MEMS fabrication prevent thick PS (>1 µm) from being used as an independent structural material in MEMS device fabrication. As will be detailed later, this is one of the key limitations which this work seeks to address.

1.2.2 Stress and stress gradient effect on PS-MEMS

As an example of the conventional application of surface micromachining, microbeam sensors have been investigated using a variety of materials, including Si, Si₃N₄ and AlN [50-52]. In addition, suspended PS structures have previously been fabricated and released [29, 53] such as that shown in Figure 1.1. However, the porosity of those films was not uniform, leading to significant bending from internal stress, made worse by the very low stiffness of the material.

Released PS microstructures can present significantly different profiles due to the residual stress. Figure 1.9(a)-(c) provides a preview of the PS microbeams fabricated in this work together with schematic plots of possible structural change due to residual stress in these microbeams. As shown in Figure 1.9(b), when PS microbeams are under compression due to compressive stress, the microbeam will show bending deformation. On the other hand, when the same PS microbeams are under tensile stress, the microbeam is expected to be flat as indicated by the model in Figure 1.9(c). Clearly stress within PS microstructures cannot be ignored if the designs depend on it so strongly.

Residual stress in these PS microstructures is critical to achieve the desired performance of micro-devices and it evolves through the entire PS-MEMS fabrication process due to various film treatments including annealing and HF immersion. While stress is known to affect the resonant frequency of bulk (non-porous) microbeams [54, 55], the impacts of stress on low modulus PS films [42, 56], beyond the obvious change to the profile suggested by Figure 1.9(b) and Figure 1.9 (c), are not yet known.
Figure 1.9  Doubly clamped PS microbeams. a) SEM image of released PS microbeams (beam voltage of 5kV), b) ANSYS model of PS microbeam under compressive stress, c) ANSYS model of PS microbeam under tensile stress. The ANSYS model was carried out assuming a non-porous material with the same Young’s modulus (1.1 GPa), Poisson’s ratio (0.09) and density (423 kg/m³) as the PS employed in a).

Figure 1.10 provides preliminary evidence obtained in this work of the effect of stress, showing released doubly clamped PS microbeams and PS microbeams broken at anchors. When the PS microbeams are under significant stress and stress gradient, failure at one end forms singly-supported fixed beams, while breakages at both ends result in complete loss of the structure. Singly-supported fixed microbeams show bending deformation due to the out-of-plane stress gradient in the microbeams. This effect can significantly alter the process yield and performance of PS-MEMS structures, so that it is important to limit the stress gradient and fabricate flat PS microstructures.
Therefore, as major factors that can significantly affect the yield and performance of PS-MEMS structures, the residual stress and stress gradient need to be considered to understand their effect on performance of structures during the design and fabrication processes. However understanding is only part of the picture - methods of controlling the stress and stress gradient are also necessary to enable this technology to move forward in the MEMS field.

1.3 THESIS GOALS AND ORGANISATION

The first goal of this work is to establish multistep micromachining processes to achieve the fabrication of scalable, complex and uniform porosity PS-MEMS structures. This requires the investigation of the mechanical properties including residual stress and stress gradient. A secondary goal is therefore to characterise PS-MEMS structures fabricated through the processes developed through this work. Through models and experimental studies, the innovative studies to be presented in this work include:

- The development of a new pore filling techniques for thick (defined for the purposes of this work as greater than 1 µm) PS which makes it compatible with standard photolithography and suitable for multilayer optical films.
- The first reported study of the residual stress evolution of PS films under different treatments that could be experienced during micromachining processes, including detailed investigation of PS stress under different annealing conditions.
• The investigation of unique methods to tune the stress and stress gradient of PS films.
• The demonstration of repeated patterning of PS structures based on standard photolithography to fabricate complex PS-MEMS structures.
• Optimisation of the electropolishing and drying process for release of suspended PS structures.
• Mechanical characterisation of fabricated PS structures, including the highest resonant frequency ever reported in a PS-MEMS device.
• Demonstration of preliminary chemical vapour sensing results using PS-MEMS based sensors.

The development and advancement of each of the above achievements are presented over five chapters. Chapter 2 reviews the current techniques for photolithography masking layers, patterning and release of PS structures with micromachining. Advantages and disadvantages of different techniques are discussed, subsequently optimised fabrication processes are established. In Chapter 3, a variety of techniques for physical and chemical characterisation of the PS films and structures are discussed, as these are fundamental to the observations to be presented. Subsequently detailed investigations of PS film residual stress evolution under various treatments are discussed in Chapter 4, which include thermal annealing, HF immersion, re-annealing and re-immersion processes. Chapter 5 presents a comprehensive micromachining process for PS-MEMS structures, designed with CMOS compatibility in mind. In Chapter 6, mechanical property analysis and characterisation of the created PS-MEMS structures are reported. Finally, chapter 7 offers the opportunity to discuss and review the major finding and some implications and possibilities for the future.
CHAPTER 2
MICROMACHINING PROCESSES FOR POROUS SILICON

In this chapter, an introduction to conventional micromachining on Si is firstly presented. Subsequently the fabrication processes necessary to achieve released micromachined porous silicon structures are discussed. They include standard photolithography utilising a pore filling technique, repeated patterning and release process through electropolishing without a sacrificial layer. For each process, a comparison of different techniques is presented, subsequently optimised procedures in PS-MEMS structure fabrication were established with the information provided by the comparisons. In addition to reviewing other work, the particular contributions of this work in PS micromachining are presented, especially the development of pore filling technique and release process. The investigation provides opportunities for scalable, complex PS microstructures fabrication based on standard photolithography, and a path towards CMOS compatible techniques.

2.1 CONVENTIONAL SILICON MICROMACHINING PROCESSES

Micromachining generally involves a series of processes to create 3-dimentional microstructures by leveraging integrated circuit fabrication processes. Micromachining to form MEMS has advantages of small size, low weight, high resolution and production scalability. Therefore, any micromachining processes to be considered must be repeatable, high resolution and designed with standard CMOS technology compatibility in mind. To understand the processes under consideration, conventional micromachining of Si substrates will be considered in this section.
A schematic flowchart of the conventional micromachining processes on Si substrates is shown in Figure 2.1. Initially, pre-treatments including cleaning and passivation are carried out on the substrate, followed by photolithography and deposition/etching prior to microstructure fabrication. For photolithography, an indispensable technique in transferring patterns to the substrate, the substrate is covered in a uniform, photosensitive films called photoresist (or simply resist). Photolithographic processes include spin coat of photoresist, ultraviolet (UV) exposure through a mask containing the designed pattern, and development to remove unwanted photoresist, leaving only patterned photoresist on the substrate.

![Figure 2.1 Schematic flowchart of conventional micromachining processes.](image)
In addition, repeated pattern transfer processes (including photolithography, etching and material deposition) are employed to create complex structures. For example, to fabricate multilayer structures with different patterns for each layer, separate photolithography, etching and/or material deposition processes are required to form each structural layer [57]. For surface micromachining which usually includes a release process to fabricate suspended structures, repeated photolithography is also required to define the released region and the etching process to remove the sacrificial layer [58].

As shown in Figure 2.2, photoresists used in the photolithography process are classified into two groups according to different exposure properties: (a) positive photoresist, for which the region of photoresist exposed to UV becomes soluble to developer, and will be removed after development; and (b) negative photoresist, for which the region of photoresist exposed to UV becomes insoluble to developer, and the unexposed region will be removed after development. A suitable photoresist needs to be selected for each photolithography process, to be compatible with the relevant masks and materials [45].

![Figure 2.2 Comparison of photolithography with two types of photoresist: (a) positive photoresist, (b) negative photoresist.](image)

Etching is the conventional technique to remove substrate regions uncovered by the masking (protection) layer. In general, etching is divided to two types based on the working principle: (1) dry etching, which removes material through reactive ion or vapour phase etchant [59] and generally includes plasma etching; (2) wet etching, which
dissolves material through immersion of the sample in a chemical etchant [60] such as KOH or HF. In addition, two different examples of cross-sectional etch profiles are shown in Figure 2.3. To achieve the isotropically etched profile as shown in Figure 2.3(a), wet etching with an isotropic etchant can be used. Alternatively, to perform a directional etch with good selectivity as shown in Figure 2.3(b), dry etching with ion milling is typically employed, such as inductively coupled plasma reactive ion etching (ICP-RIE) and deep reactive ion etching (DRIE). In such etching, the directionality is defined by the patterning and exposed areas. Directional etching can also be achieved on crystallographic substrates using directional etchants such as KOH which has a different etch rate for each silicon plane. After etching, removal of residual photoresist is typically carried out by either acetone immersion or plasma ashing [61, 62], leaving a cleaned, patterned Si surface as defined by the mask.

**Figure 2.3** Two different examples of cross-sectional etch profiles: (a) isotropic etching; (b) directional etching.

An illustration of the photolithography and etching process to form microstructures on bulk Si is shown in Figure 2.4. After spin coating of negative photoresist on top of the Si substrate (Figure 2.4(b)), exposure through a mask is carried out to transfer the pattern on to the photoresist (Figure 2.4(c)). After developing to remove unexposed negative photoresist, a photoresist pattern will be formed on top of the Si substrate (Figure 2.4(d)), which protects the Si underneath from being attacked during the etching
process. In Figure 2.4(e), the Si has been etched to form a patterned Si microstructure with the reverse pattern to the mask, after residual photoresist has been removed.

For surface micromachining to create released microstructures, a sacrificial layer and repeated patterning are generally employed. Figure 2.5 demonstrates the conventional surface micromachining processes on Si for doubly clamped microbeams. Firstly a sacrificial layer is deposited and patterned on top of the Si substrate, as shown in Figure 2.5(a). Features are etched (patterned) in the sacrificial layer all the way to the Si substrate, as this forms the anchors of the supporting structure. Subsequently the structural layer is deposited and patterned on top of the sacrificial layer, as shown in Figure 2.5(b). Both patterning of the sacrificial layer and of the structural layer can be carried out with standard photolithography and etching as discussed before and outlined in Figure 2.4. Finally, the sacrificial layer is removed through another etching step, leaving (in this case) released doubly clamped microbeams on top of the substrate, as shown in Figure 2.5(c).
Figure 2.5 Conventional micromachining on Si to release microstructures. (a) After deposition and patterning of sacrificial layer; (b) After deposition and patterning of structural layer; (c) After removal of sacrificial layer to release the microstructure.

Using micromachining processes, scalable, complex microstructures based on Si can be fabricated with high resolution. However, the goal of this work is to use PS as a structural layer which is particularly difficult due to the low rigidity (Young’s modulus on the order of 1 GPa for P=80%, compare to Si Young’s modulus of 163 GPa [4]) and high chemical reactivity of the films. As a result, a detailed understanding needs to be obtained in regards to how to process these films, to allow the porous films to be micromachined in a manner which could eventually lead to compatibility with current micromachining processes. A review of these processes will be detailed in the following sections.

2.2 MASK MATERIALS FOR PATTERNING ON POROUS SILICON

As an indispensable process of micromachining, patterning is critical to fabricate complex structures such as multilayer or released PS-MEMS structures. To implement
patterning, an initial masking layer is patterned by photolithography on the PS film. Subsequently additional processes can be carried out using this masked PS film to complete the PS patterning, including chemical treatments, RIE etching and ashing. In addition, patterned masking layers can be formed using either a conductive mask or insulating mask, for which the additional processes are different according to the different type of masking layer. Though different masking layers for Si patterning have been investigated [63], their compatibility with repeated patterning on PS has not be reported.

In this work the effect of both conductive (metal) and insulating (polymer, SiO₂, SiNx) masks on the patterning of PS layer have been considered. The patterning process and applicability of each mask are significantly different, which will be discussed in this section.

2.2.1 Conductive mask

A conductive mask typically refers to one layer or a multilayer of conductive metal or alloy. These have been used for PS annodisation as some noble metals are HF-resistant, such as gold (Au) and platinum (Pt) [64]. However, almost no application of conductive masks in repeated patterning of PS have been reported. Therefore, the applicability of conductive masks to patterning on PS layer will be considered in this section.

In standard microelectronic processing, the formation of a conductive mask layer typically employs a lift-off process. Such an approach is illustrated in Figure 2.6 for use on PS. Firstly the photoresist pattern with deliberately sloped sidewall is formed through standard photolithography. To obtain the sloped sidewalls, undercut is enhanced using adjusted exposure or developing time, such as over developing of negative photoresist pattern [50], as shown in Figure 2.6(a)-(b). Subsequently a layer of metal is deposited uniformly over the photoresist pattern as shown in Figure 2.6 (c), which is typically carried out by thermal evaporation or E-beam deposition. After metal deposition, an acetone immersion is used to remove the photoresist (and therefore metal on the surface of it), leaving a metal pattern on the PS only where there was no
photoresist, as shown in Figure 2.6 (d). The sloped sidewall of photoresist undercut renders it easier for acetone to reach the photoresist and remove it. For faster removal of photoresist, heating and ultrasonic vibration are typically used, or N-Methyl-2-pyrrolidone (NMP) or dimethyl sulfoxide (DMSO) can replace acetone to remove cross-linked photoresist. However, these treatments can result in mechanical damage of PS structures (heating/ultrasonic vibration) or introduce unwanted residual toxic material (NMP) in to the pores.

![Figure 2.6 The metal layer patterning on PS.](image)

(a) Exposure of photoresist, (b) after development of photoresist, (c) after metal deposition, (d) after lift-off of photoresist.

The mask formed with the above technique has very steep re-entrant sidewalls compared to that of a regular photoresist mask, which renders fabrication of high quality patterns possible through selective anodisation or RIE. However, the metal mask is extremely difficult to remove once deposited. For example, metals such as Au can only be removed by selective gold etchants (Transene Inc., USA), and the metal etchants can damage the PS film and cause contamination from ions such as iodine and potassium.
Furthermore, as shown in Figure 2.7(a)-(b), in the electropolishing process which is designed to remove Si in the area uncovered by the mask, a metal layer on top of bulk Si could form isotropic etching as shown in Figure 2.7(a). However, for electropolishing on PS-covered-Si, the PS layer cannot prevent the HF etching Si under the edge of the mask, resulting significant undercut as shown in Figure 2.7(b).

**Figure 2.7** Comparison of electropolishing with metal mask on different materials. (a) Metal mask on bulk Si, (b) metal mask on PS-covered-Si.

Such etch undercut can cause a detachment of the metal/PS layer from the substrate if it is significant. In addition to the above problems, this type of mask can also have an impact of the electropolishing process on PS, causing excessive etching under metal/PS layer.

The observation then is that a metal mask is suitable for applications that do not require the removal of the metal layer, which includes applications requiring electrical traces or optically reflective surfaces. Figure 2.8 shows an example of a patterned PS film and the metal layer used for release of some of the PS microbeams fabricated in this work. A layer of Cr/Au (10nm/200nm) was deposited on the surface of the PS anchors through thermal evaporation and lift-off processes. The metal masking layer protected the
anchor regions in the subsequent release step, but was not removed after release of the PS microbeams. Furthermore, significant under mask etching occurred during the electropolishing release step, causing detachment of the metal/PS layer.

![Metal mask patterned on top of PS microbeam anchors. Beam voltage of 5 kV.](image)

**Figure 2.8** Metal mask patterned on top of PS microbeam anchors. Beam voltage of 5 kV.

### 2.2.2 Insulating mask

In contrast to conductive metal masks, insulating masks of various materials have been extensively studied and reported for PS patterning. Investigated materials include thermally deposited masks of SiO$_2$ or Si$_3$N$_4$[65], polycrystalline Si [66, 67], bilayers of polycrystalline Si/SiO$_2$ [68], Si$_3$N$_4$, SiC or bilayer of Si$_3$N$_4$/SiO$_2$ [64]. For the different materials used, the corresponding anodisation, electropolishing or plasma etching processes must be different to ensure compatibility with the masking layer used. However, these types of masks generally require a multistep removal process, and the etching for PS is not selective for some mask materials such as Si$_3$N$_4$ or SiC [64]. Further chemical or physical etch removal processes can cause detachment of the mask and undermine the quality of PS structure.

Thick SU8 photoresist is another popular insulating mask material, however it is a highly crosslinked epoxy that cannot be easily removed by standard stripping chemicals. So complex aggressive processes including ultrasonic treatment during stripping are generally needed [69]. Due to the very low Young’s modulus (on the order of 1.0 GPa for 80% porosity) of the PS films considered here, the use of ultrasonic baths has the
potential to damage the porous silicon structures. Furthermore, where hard masks (with high Young’s modulus) such as Si₃N₄ or SiO₂ are utilised, even a small amount of residual stress (20 MPa is common in thin films deposited on silicon) would lead to significant strain in PS.

Conventional photoresist has been reported to work as a masking layer for PS formation on Si substrates [63], and can also serve as an insulating mask for repeated patterning on PS. However, the use of photoresist films according to manufacturer’s specification cannot withstand the attack of high concentration HF solution (>25%) for longer than 10 min, otherwise pinholes emerge in the masked area [26, 63]. This limits the use of photoresist masks in subsequent processes that require long immersion in HF solution, such as long term anodisation/electropolishing.

A new technique employing fluoropolymer (FP)-based mask layers was reported recently [70]. Such layers are reported to be highly chemical resistant to HF-based electrolyte and allow damage-free removal under O₂ plasma ambient. However, this technique requires a SiO₂ hard mask deposition step to cover the fluoropolymer for patterning, complicating the process and introducing potential PS film oxidation. Oxidised PS will not only lower the refractive index of the film, but also leave the film under significant compressive internal stress, which can cause film cracking or, in the case of PS-MEMS, device failure. Therefore, this process is not ideal for applications which try to avoid film oxidation or achieve low internal stress of fabricated structures.

In conclusion, for PS patterning, although a significant number of materials exist which can be used as a mask, standard photoresist is still the most convenient and effective option for application of insulating mask, as long as the photoresist is compatible with chemicals such as HF to be used. In this work, repeated patterning is employed for selective area electropolishing of PS structures. Generally, immersion in 5% HF/DI electrolyte for a maximum of 3 minutes is required during the electropolishing release steps for PS films (up to 2.5 μm thick) in this work, which does not cause a significant degradation of the photoresist mask. Figure 2.9 shows an example of the photoresist masking layer used in this work, patterned on top of PS layer and immersed for
3 minutes in 5% HF/DI. The photoresist exhibited good HF resistance for this short immersion period, and it could be removed with a simple acetone immersion afterwards.

![Figure 2.9 Photoresist mask on top of PS layer. Beam voltage of 15 kV.](image)

### 2.3 PATTERNING OF POROUS SILICON FILM

Patterning of PS film based on standard photolithography is the first and indispensable step for making complex PS-MEMS structures. However, due to the porous structure and large surface area of PS, photoresist can easily seep into the pores during spinning and adhere to the Si skeleton of the PS. UV light has a very short penetration depth into Si (~10 nm), and for PS, the maximum penetration depth is estimated to be on the order of 100 nm at a wavelength of 365 nm [71, 72]. The short penetration of the light results in a very limited exposure of the photoresist in the pores, leaving only a small amount of photoresist below the PS surface exposed. For positive photoresist, unexposed photoresist deep into the porous film not be removed and will adhere to the pores after the standard soft/hard bake process. For negative photoresist, a long development time is needed to remove unexposed photoresist from pores under the photoresist pattern, but this will result in a photoresist pattern with significant undercut which can detach from the substrate.

Furthermore, photoresist which seeps into pores will significantly affect subsequent processes. For additive processes such as metal deposition, metal covered regions of the PS will be affected by the photoresist seepage as the metal layer prevents the removal of photoresist. For subtractive processes such as dry etching, the residual photoresist in porous silicon can slow down the etch rate significantly and result in a
rough surface etch due to the etch rate difference between the photoresist and Si [45, 73]. Therefore, the photoresist in the pores becomes a noticeable hindrance in achieving well defined PS features patterned with photolithography.

Pore filling techniques, which utilise a layer of material to fill the PS pores before spin coating of photoresist, are used to address this patterning issue in PS films. Figure 2.10 shows the comparison of photolithography on PS without pore filling material (a) and with pore filling material (b) at different stages of the photolithography process. At stage (II), the photoresist seeps into pores of PS when there is no pore filling material utilised prior to the coating with photoresist, as shown in Figure 2.10(a). However, when the PS layer is filled with a pore filling material prior to the coating with photoresist, conventional photolithography can be implemented on the surface of the sample, as shown in Figure 2.10(b). At stage (III), in Figure 2.10(a), after developing to remove the exposed photoresist, significant photoresist residual is present in the PS layer. In contrast, when the pores are filled with pore filling material, which would be removed after the developing, the PS layer will be left unaffected, as shown in Figure 2.10(b).

Figure 2.10 Comparison of photolithography on PS, (a) no pore filling material is utilised prior to coating of photoresist, PS is filled by photoresist, (b) a layer of pore filling material is utilised prior to coating of photoresist. (I) PS layer formed on Si substrate; (II) UV exposure; (III) after developing to remove exposed photoresist.

Previous studies in Microelectronics Research Group have developed a N₂ annealing technique to form a thin SiOₓNᵧ passivation layer on the PS pore surface, preventing
further oxidation and enhancing the resistance of PS to alkaline developer [39]. This technique renders the PS film compatible with standard photolithography. However, when this technique was initially developed, comprehensive procedures for fabricating scalable, complex PS-MEMS structures were not established due to the limitation of the pore filling technique utilised, when patterning thick PS films (>1 µm). This will be discussed in detail in Section 2.3.2.

In the following sections, PS film fabrication and passivation in preparation for further processing will be discussed, along with pore filling techniques and patterning methods. Optimised techniques in completing each stage of the PS patterning process will be presented.

2.3.1 Film formation and passivation

To achieve PS layers with laterally uniform porosity, PS is normally formed via the partial electrochemical dissolution of crystalline silicon in HF/Ethanol solution [6]. This technique is used throughout this work. The porosity of the PS layer is determined by the HF concentration and anodisation current density while the thickness is controlled by anodisation time and pore formation rate [40].

Importantly, for a laterally uniform films, the electric field and HF concentration must be uniform across the surface. Hence any techniques that pattern the surface before PS formation (as shown in Figure 1.7(d) and Figure 1.8) lead to laterally non-uniform films. As porosity determines the density, Young’s modulus [4] and refractive index [5] of the film, any non-uniform porosity distribution would introduce non-uniform physical or optical properties as mentioned. This will significantly affect the device quality when using PS as the structural layer.

A single-tank anodisation cell, as shown in Figure 2.11, was employed to fabricate the PS samples in this work. The single tank anodisation cell has the advantages of simple setup and convenient control of the parameters. To achieve a uniform distribution of electric field, the cell includes a spiral platinum (Pt) cathode and an aluminium (Al) plate connected to the anode of constant current source. A conductive elastomer (Zoflex, CD45.1, 1.5 mm thick) is placed between the Al plate and the Si wafer, to
provide a conformal, temporary and non-destructive electrical contact [40]. In addition, the anodisation is undertaken under dark ambient light conditions through covering the cell opening, to keep current density stable [74, 75]. All the design features listed above guarantee a high quality PS layer with laterally uniform porosity will be formed on top of the Si wafer.

![Figure 2.11 Single-tank anodisation cell for PS formation.](image)

For research consistency and comparison of PS properties, the samples used in this work were all formed on 2-inch diameter p-type double side polished Si (100) wafers with resistivity of 0.9±0.2 Ω·cm (Boron doped, doping density of 2.5×10^{17} cm^{-3}), resulting in a PS area of approximately 10 cm² (3.0 cm diameter) on one side of the Si wafer after anodisation. After PS formation the samples were rinsed in DI water and blow dried with N₂. In this work, room temperature anodisation was performed in a 15% HF/ethanol solution, unless otherwise specified. The HF and ethanol were measured through a pipette to ensure the accuracy of solvent ratio in electrolyte. Different current density and anodisation time were used to form PS layers with the same physical thickness of \( t = 2.5 \pm 0.1 \) μm, but with a range of porosity \( P \) from \( P = 71\% \) to \( P = 87\% \).

SEM images of plan view of the top surface and cross-sectional view of as-fabricated PS film typically utilised in this work are shown in Figure 2.12(a)-(b). The average pore size of the PS is estimated to be less than 10 nm, indicating the PS is categorised as meso-porous (pore size ranging from 2-50 nm). This type of PS has advantages of large surface area compared with bulk silicon as estimated from Figure 1.5 and a large volume-to-surface area ratio of around 180 m²/cm³ [76], low optical absorption and
Chapter 2

scattering losses in the infrared [45], and isotropic mechanical, electrical, optical and thermal properties, which render it a suitable PS material for fabrication of chemical/biological sensing and optical microstructures.

![SEM images of as-fabricated meso-porous PS](image)

**Figure 2.12** Examples of SEM images of as-fabricated meso-porous PS utilised in this work. (a) Plane view of the top surface of PS; (b) cross-sectional view of PS; (c) detailed porous profile of (b). Beam voltage of 0.5 kV.

For highly doped p-type silicon, a very thin (80 nm for 1 µm thick PS) parasitic surface layer on PS has been observed [77, 78], this surface parasitic layer will hinder diffusion of reactive species and thus affect formation of PS in the out-of-plane direction. The presence of this parasitic layer could also affect the absorption of particles in PS sensing application. In this work, a parasitic surface layer of thickness <200 nm was observed for a 2.5 µm thick PS film in Figure 2.12(b). This would not significantly affect the mechanical properties (stress, Young’s modulus, Poisson’s ratio) of PS or the behaviour in sensing applications, therefore the parasitic layer was not taken into account. In addition, processes to inhibit the formation of the parasitic top layer have been reported [79], which could be implemented to effectively avoid the formation of a parasitic surface layer during anodisation.

To make PS film suitable for alkaline developer [39] or to study the annealing conditions of the PS film [80] (details will be discussed in Chapter 4), rapid thermal annealing under N₂ was performed on the majority of samples. The annealing enables the formation of SiOₓNᵧ passivation layer on the surface of PS. The transferral time between anodisation and rapid thermal annealing was controlled to be less than 3 min to limit any film changes due to ambient oxidation.
A cross-sectional diagram of the rapid thermal processor and the chamber temperature evolution along with time are illustrated in Figure 2.13(a)-(b). As shown in Figure 2.13(a), the PS sample is held in a silicon carbide coated graphite susceptor (diameter of 4 inches) during the annealing in the rapid thermal processor (AS-One 100 from ANNEALSYS Inc.). The susceptor is covered with a silicon wafer to provide an isothermal environment and highly uniform temperature across the sample [45]. The gas inlets of the processor are located below the quartz window in front of a halogen lamp which heats the incoming gas stream and avoids any thermal gradient due to gas circulation on the susceptor during the process. Pyrometers are installed under the centre and edge of susceptor for temperature monitoring and control.

For the annealing process as shown in Figure 2.13(b), the annealing chamber is firstly cleaned through a vacuum/purge with high purity (99.999) N₂ gas for three cycles, which removed any residual water and oxygen before increasing the temperature, to avoid thermal oxidation of the sample. Subsequently the temperature was ramped at a rate of 20 °C to reach the preset annealing temperature and kept stable during the process (typically 600 °C, 6 min, at the flow rate of 1000 sccm in this work). When the annealing process was finished, the chamber was cooled through a purging gas (N₂) and external water cooler.

All the PS-MEMS fabrication studies in this work used PS films annealed in this way, as it has been previously comprehensively studied and developed as a suitable passivation process [39, 40]. For the film stress investigations carried out in Chapter 4, in addition to N₂ annealing conditions, comparisons were also made with samples annealed in different gas environments or kept in a vacuum of 10⁻⁶ Torr.
Figure 2.13  Annealing processor and the chamber temperature evolution during the process. (a) Cross-sectional illustration of rapid thermal processor AS-One 100 for annealing of PS. (b) Plot of annealing processor chamber temperature (as measured by pyrometers) evolution with time.

2.3.2 Pore filling techniques

Different pore filling materials have been reported, including Ge/Si [81], SiO$_2$ [14], dielectric material [82] or metal [83]. Pore filling with these materials has been carried out through chemical vapour deposition (CVD) at a slow rate or through immersion of the PS in a metal salt solution, resulting in the porous structures being permanently filled. However, these methods require complex patterning and are a time consuming deposition processes. Furthermore, removal of the deposited materials is extremely difficult and easily induces physical change of the PS films.
ProLIFT (ProLIFT100, Brewer Science Inc.) has been used for pore filling during the photolithography process in previous work [49]. It can be spun into PS before application of the photoresist, and can be removed by standard TMAH (TetraMethylAmmoniumHydroxide) based developers such as MIF326 or MIF826 (MicroChemicals GmbH, Germany). However, when this photolithographic technique is applied to thick (>1 µm) PS films, the use of ProLIFT is limited. ProLIFT is not photosensitive and is typically removed by alkaline based solution such as developers. However when the PS is thicker than 1 µm, excessively long developing time is required to thoroughly remove the ProLIFT in the entire PS layer, resulting in degradation of the photoresist pattern and damage to the PS structure. Furthermore, standard ProLIFT100 needs to be diluted to infiltrate deep into PS layers, and the dilution and spin coat processes are difficult to control when the PS porosity and/or layer thickness changes. Therefore in this work a new material, Spin-on Glass (SOG) (700B, 10.8% SiO₂ content, Filmtronics Inc, USA) was investigated as a replacement for ProLIFT, as a pore filling material, which was suitable to fill pores of PS films (typically with P=71-87%, t=2.5 µm) used in this work.

SOG is a type of liquid based organic silicate which can be subsequently transformed to silicon dioxide (SiO₂) through heat treatment. In the microelectronics industry, SOG is typically used as diffusion source or a planarising dielectric for multilevel metallisation schemes in the fabrication of modern integrated circuits [84, 85]. Because the resulting thin SiO₂ films or coatings can be easily removed through HF immersion or C₂F₆ plasma etching, SOG has also been used as a sacrificial layer in the integrated circuit industry [86].

To understand the improvement in using SOG over ProLIFT, a comparison of the ProLIFT and SOG pore filling process is depicted schematically in Figure 2.14, at three steps in the patterning process: (I) UV light exposure with photoresist patterning; (II) development to remove exposed positive photoresist; (III) reactive ion etching (RIE) and photoresist/pore filling material removal. While ProLIFT is used to fill the PS pores prior to the application of photoresist in step (I), it is not UV sensitive and is only removed by standard alkaline developer during the photoresist development step. While this was considered advantageous as it allows ProLIFT to be patterned in the
same wet process that defines the photoresist, it intrinsically links the development time of the photoresist and the ProLIFT (pore filling) removal time. Since the underlying goal of introducing pore filling is to achieve high quality patterning and the patterning process requires accurate control of the developing time, this linking of times leads to issues. If the developing time is too short, exposed photoresist will be removed but ProLIFT residue will remain in the PS film, slowing the RIE removal of PS, as shown in Figure 2.14 (a). Furthermore, any residual ProLIFT in the PS film once released is expected to introduce stress in released microbeams, resulting in beam breakage (poor yield). On the other hand, if the developing time is too long, the photoresist will be overdeveloped, causing a sloped side wall angle of the photoresist pattern, resulting in poorly defined PS structures as shown in Figure 2.14 (b). Worse, over developing can result in lift-off of the patterned photoresist if it is not well attached to the PS film.

Repeated experiments have shown the developing time becomes a significant issue when patterning PS films above 1 μm thick, as they require a much longer developing time (> 60 s) to remove all the ProLIFT in the PS films than typically required for photoresist development (~30 s).

By comparison, when considering spin-on-glass (SOG), SOG is used to fill the pores of PS at step (I) of Figure 2.14, which is not removed during the developing process at step (II). This guarantees the accurate control of developing time for the photoresist layer, resulting in well patterned PS structures at step (III), as shown in Figure 2.14 (c). SOG is then removed by HF immersion after formation of the photoresist pattern. A 10 s dip in 10% HF/ethanol solution was confirmed by testing to be sufficient to remove all SOG in an exposed PS film (where there was no photoresist) up to 2.5 μm thick. The short HF dip resulted in an optical thickness change of less than 4.4%, suggesting the short immersion had very little effect on the PS layer. Furthermore, the N₂ annealed PS will not significantly change its resistance to developer even after long immersion (80 s) in HF solution [45], so repeated immersion in HF and anodisation can be carried out.

In this work, which used PS layers of 2.5 μm thickness, SOG as a pore filling layer was more advantageous than ProLIFT and was used as described above. Therefore, the
application of SOG as a pore filling material renders relatively thick (>1 µm) PS film available for fabrication of microstructures using standard photolithography. This technique guarantees accurate control of exposure and developing time, significantly improving the quality of patterned PS structures thicker than 1 µm. In addition, SOG is commonly available within the microelectronics industry, moving the process a step closer to achieve a scalable PS-MEMS technology.

2.3.3 Photolithography and reactive ion etching

The N\textsubscript{2} ambient passivation process discussed in Section 2.3.1 renders PS layers suitable for standard photolithography process using alkaline based developers, and the pore filling technique based on SOG ensures high resolution photolithographic pattern transfer onto relatively thick PS films. The two techniques modify the PS layer to be a robust material enabling a path towards integration with CMOS compatible processes. Both positive photoresist and negative photoresist can be applied on PS with the SOG pore filling technique discussed in Section 2.3.2. However, when transferring the photoresist pattern onto the PS (by dry etching), the thickness of the photoresist can significantly affect the sidewall angles of the patterned PS structures, as shown in Figure 2.15 (corresponds to stage (II) and (III) in Figure 2.14(c)). By decreasing
photoresist thickness, a significantly more vertical sidewall can be achieved in the patterned PS structure.

![Diagram showing comparison of thick and thin photoresist sidewalls](image)

**Figure 2.15** Comparison of patterned PS structures after dry etching, for photolithography carried out with positive photoresist with (a) thick photoresist, (b) thin photoresist.

The photoresist thickness has very significant implications for technologies which require steep sidewalls. For example, PS gratings which were fabricated in this work are shown in the scanning electron microscope (SEM) images in Figure 2.16. The structures were fabricated with SOG assisted photolithography discussed in Section 2.3.2 and RIE processes. For PS grating sidewalls which were designed to be vertical, the shallow incline changed the duty cycle of the gratings and compromised the diffraction efficiency [87], especially for small structures which had an aspect ratio (height of PS : width of PS) higher than 1:1. Similar observations are true for PS waveguides and couplers [88] where imperfect side walls can affect the number of supported modes and scattering losses.
To address this issue, a thin layer of photoresist was required to pattern the underlying pore-filled PS and to complete the photolithography in the first patterning process. Specifically, standard positive photoresist AZ6632 (35% solids content, MicroChemicals GmbH, Germany) was diluted by AZ EBR solvent (MicroChemicals GmbH, Germany) which lowered its viscosity. Lower viscosity photoresist achieves a thinner masking layer after high speed spinning of the resist onto the substrate. The thinned photoresist with a 20% solids content resulted in a typical photoresist pattern thickness of approximately 0.85 μm; reduced from ~3.4 μm for the undiluted photoresist at the same spin speed. This thinned photoresist was used later in PS-MEMS structures fabrication in Chapter 5.

An optimised ICP-RIE process has been established by Lai et al. [73] to rapidly etch (~1 μm/min for the as-fabricated PS in this work) the PS film in the region not covered by photoresist, to form the patterned PS structures. The ICP-RIE etching conditions used a gas mixture of CF₄/CH₄ (31 sccm / 3 sccm) at a temperature of 25 °C. The etch rate of annealed PS and the sidewall angle of the etched structure in relation to chamber
pressure are shown in Figure 2.17 [45]. By comparison the etch rate of single crystal Si is 15 to 27 times lower than that of PS. In this work a chamber pressure of 80 mTorr was used to achieve vertical sidewall angle according to the data shown in Figure 2.17.

Figure 2.17  The etch rate of annealed PS and the sidewall angle of the etched structure. *Image taken from [45].*

If the SOG in the uncovered PS has not been totally removed, the RIE rate will decrease significantly, which results in a much longer etching time to remove the PS film (closer to that of the photoresist etch rate), providing a process indicator of how thorough the SOG removal from the pores has been achieved. After RIE, the positive photoresist could be removed by a 5 min acetone immersion, leaving the patterned PS structure on top of the Si substrate largely unaffected by the etch process.

### 2.4 RELEASE OF POROUS SILICON STRUCTURES

Surface micromachining, which is characterised as micromechanical structure fabrication from thin films deposited on the surface of a substrate, has been widely used and integrated with CMOS circuits since the 1960’s [89]. For surface micromachining, the release of microstructures from the substrate is critical and often determines the success of the whole process.
Due to the large surface area, as-fabricated PS can dissolve rapidly at room temperature in dilute hydroxide solutions such as KOH, NaOH and NH₄OH, rendering it an ideal material for use as a sacrificial layer in release processes [25, 26]. However this work is concerned with utilising PS as the structural layer for the MEMS device and not the sacrificial layer. Instead the use of electropolishing combined with anodisation to create released PS-MEMS devices is proposed and demonstrated.

In surface micromachining, a sacrificial layer is typically used under the structural layer to release microstructures, as shown in Figure 2.5. This technique has been employed in PS structure release as well, where PS structures formed using stain etching of silicon on insulator (SOI), buried oxide (BOX) was used as a sacrificial layer and removed by wet etching in HF solution to release the structures [90]. In another study, a high-density plasma reactor was employed to isotopically laterally etch the bulk Si substrate and release a PS microplate (50×50 µm²) using an Alcatel micromachining etching tool (MET) [91]. However, the process was complicated and significant undercut occurred due to the isotropic etching.

A Bosch-proprietary “advanced porous silicon membrane (APSM)” process has been reported [1, 92, 93], which employed nano-porous silicon as an auxiliary layer during the fabrication of a monocrystalline silicon membrane covering a vacuum cavity, to fabricate MEMS pressure sensors. However, in this process PS was thermally rearranged during the cavity sealing and Si membrane creation processes, and was not utilised as a structural layer in the MEMS sensor.

Finally, electropolishing with constant current or pulsed current to etch the Si substrate has also been reported [42, 94, 95]. This technique can be carried out using the same apparatus that is used for PS formation, which avoids complex processes and enables release of PS using standard photolithography techniques. These advantages render electropolishing to be the most convenient option for release of PS structures and was used in this work. A unique feature of this work is that the uniform porosity and use of electropolishing produces optically flat surfaces that would enable high quality optical devices to be fabricated and released.
2.4.1 Electropolishing

PS formation and electropolishing occur at specific current densities and HF solution concentrations [96, 97]. To help understand the effects of current density and HF concentration, the current - potential curves of dissolution of p+ Si sample in HF are shown in Figure 2.18(a)-(b).

![I-V curves of dissolution of p+ Si sample in HF](image)

**Figure 2.18 I-V curves of dissolution of p+ Si sample in HF.** (a) I-V relationship showing the different regions of dissolution, in 1% HF, (b) effect of HF concentration on the I-V curve (images adapted from [96]).

For the PS formation technique with anodisation, low current density and high concentration HF/ethanol solution are used, while during electropolishing, high current density and low concentration HF/DI are required to achieve the critical
electropolishing conditions [98]. For the Si substrate utilised in this work, the typical electropolishing conditions are: current density \( \geq 15\text{mA/cm}^2 \), and HF concentration in deionized water of less than 5\%. However, it was found that the critical electropolishing conditions were strongly linked to the mask material and patterned area used for electropolishing:

1) Compared to an insulating mask, a metal mask requires higher current and/or lower HF concentration to achieve an electropolishing condition, as the metal mask region draws current through it, which decreases the current flow from the uncovered region.

2) As the area of regions covered by the mask increases at the same applied current, the local current density will increase in uncovered regions. This drives the system further into the electropolishing region, which then requires a lower current density and/or higher HF concentration to achieve electropolishing.

This latter point is important as during electropolishing, lower current density and higher HF concentration of electrolyte result in less energetic reactions during removal of the uncovered Si, which helps avoid breakage of the released PS structures and therefore increases the yield. Further, etch rates will change with current density. As the electropolished region forms the released height, it is important to well understand and control the critical current density to achieve reproducible release heights.

### 2.4.2 Photoresist mask adhesion enhancement

For long immersion times (>10 min) in HF solution, there is the potential of producing pinholes in the photoresist mask, leaving the mask and underlying Si vulnerable to attack by HF [26, 63]. This process would significantly degrade the integrity of the photoresist mask, resulting in either pinholes or a long undercut during anodisation/electropolishing and making it easier for the photoresist/PS layer to delaminate from the Si substrate. Therefore, when long immersion in HF solution is required to form a relatively thick PS layer or large release gap through electropolishing, the adhesion between the photoresist and substrate needs to be enhanced.
A method employing thick (10 µm) negative photoresist AZ9260 (MicroChemicals, Germany) has been reported for anodisation of PS film on Si [99], which included a 15 min interval of resting in air before a soft-bake, and a 2-hour long hard bake of the patterned photoresist, in order to harden the photoresist and avoid bubbling. For p-type Si substrates, this method was found to significantly enhance the robustness of the photoresist mask, allowing it to withstand an anodisation time of up to 30 min.

In this work, to ensure photoresist seepage into the pores of the PS film and enhance the adhesion between photoresist and substrate, diluted AZ6632 (solid content 20%) was spun twice on the sample, followed by a 2-hour hard bake at 100 °C, which aimed to avoid bubbling and delamination of photoresist from substrate. This resulted in a typical photoresist thickness of 1.5 µm on top of PS film. Compared to the technique reported in [99], the photoresist adhesion enhancement technique in this work was applied with different photoresist and resulted in thinner photoresist making layer, in addition, this technique was utilised for electropolishing of PS-over-Si but not PS formation.

### 2.4.3 Drying process

As discussed at the start of Section 2.1, wet or dry etching is typically used to release MEMS structures from the substrate. Generally the etch methods include an isotropic or anisotropic etch to produce a cavity under the MEMS device or remove a sacrificial layer. At the conclusion of the wet etching process (such as electropolishing utilised in this work) the suspended structures that have been formed are kept submerged in liquid-phase etchant. A drying process is then required. However, during drying, the rinsing liquid trapped in the small gap (capillary-like dimensions, typically on the order of micrometres) between MEMS structure and substrate will create a strong capillary force (stiction). The capillary force is directly proportional to the surface tension of the rinsing liquid and will cause the microstructures to stick to the substrate, as shown in Figure 2.19 [100]. Therefore, if not carefully dried, structures will adhere to the substrate or even break, resulting in a low process yield.
Figure 2.19 Schematic of the cantilever beam stiction by capillary forces. Image taken from [100].

For conventional micromachining based on non-porous materials such as Si, various techniques have been reported to avoid stiction and improve the drying yield.

Firstly, different drying methods have been investigated. A comparison of major drying methods carried out for drying of Si microstructures is listed in *Table 2-1* [101]. The outcomes of the study provide various options for drying of PS-MEMS structures and achieving high yield. Due to the large surface area and low Young’s modulus of PS films, the drying process should involve as few steps as possible, to avoid potential damage to the PS sample during transfer. Therefore, evaporation and supercritical point drying are considered the best methods among all these options to achieve a high yield, release PS micromachined device.
<table>
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<th>Evaporation drying</th>
<th>Sublimation drying</th>
<th>Supercritical drying</th>
<th>HF vapour phase etching</th>
<th>Self-assembled monolayer coating</th>
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<td>HF $\rightarrow$ DI water $\rightarrow$ methanol $\rightarrow$ t-butyl alcohol</td>
<td>HF $\rightarrow$ DI water $\rightarrow$ methanol $\rightarrow$ p-dichlorobenzene</td>
<td>HF vapour $\rightarrow$ DI water $\rightarrow$ H$_2$O$_2$ $\rightarrow$ DI water $\rightarrow$ DI water $\rightarrow$ IPA $\rightarrow$ CCl$_4$ $\rightarrow$ OTS $\rightarrow$ IPA $\rightarrow$ DI water</td>
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<td>Surface tension (mN m$^{-1}$)</td>
<td>72.88@25°C</td>
<td>22.65</td>
<td>20.17</td>
<td>N/A</td>
<td>1.16</td>
</tr>
<tr>
<td>Advantages</td>
<td>Simple</td>
<td>Lower surface tension than DI water</td>
<td>Fast sublimation</td>
<td>Only hot plate needed</td>
<td>Clean; excellent results</td>
</tr>
<tr>
<td>Disadvantages</td>
<td>Mediocre results</td>
<td>Mediocre results</td>
<td>Request refrigeration and vacuum; absorbs water vapour</td>
<td>Toxic; needs vacuum contracts upon solidifying</td>
<td>Excellent results</td>
</tr>
</tbody>
</table>

*Table 2-1 Comparison of release method. Adapted from [101].*
An in-depth investigation of evaporation drying techniques for SiO₂ microbeams has also been reported [102]. Compared to the common evaporation drying methods listed in Table 2-1, a new technique was suggested to achieve optimised results. The investigation showed that a long immersion in boiling methanol and a rapid heating via rapid thermal annealing at 500 °C could increase the yield. However, this method includes multiple occurrences of sample transferral between different apparatus, and requires complex heating treatment, making the process complicated and has the potential to damage PS structures during transfers. Tests carried out in this work to trial this method did not achieve a significant improvement for the yield of PS microbeams, which could be due to the low Young’s modulus of PS of around 1 GPa. The out-of-plane rigidity of a thermal oxide microbeams (for which the process was originally intended) is on the order of 70 times larger than for the high porosity films of the same thickness. Hence, even a small amount of adhesion energy can cause damage to porous film microstructures during the drying process which affects the yield.

Critical point drying typically employs CO₂ and low surface tension liquids to complete the drying process. The liquids are required to be both water and CO₂ miscible, to serve as the intermediate fluids between the two. Generally ethyl alcohol or acetone can be employed. The evolution of pressure and temperature during critical point drying is illustrated in Figure 2.20 [103]. The sample is first transferred to a processing chamber which is filled with an intermediate fluid, then liquid CO₂ is introduced to fill the pressurised chamber with the intermediate fluid is completely removed (at point A). Subsequently, the supercritical temperature (~32 °C) of CO₂ is achieved under a particular pressure, resulting in CO₂ transforming from a liquid to a gas phase (from point A to point B). Finally with the vent of CO₂ gas and return of the pressure to an atmospheric level, microstructures can be successfully dried and released from the substrate (point C).
This technique requires minimum transferral of the sample and all introduced liquids are completely removed through the process. It also completely avoids the condensation that would result in gas returning to the liquid phase during the process [104]. Extremely high yield of microstructures can be achieved due to the simple and clean working process and the process is standard in MEMS foundries. Therefore, compared to other drying methods, CO₂ critical point drying is considered the best choice to achieve high yield porous silicon micromachined devices.

Another consideration to achieve high yield PS micromachined devices is the inclusion of structures for antistiction. Several design approaches have been reported for increasing yield and avoiding stiction, including the use of short cantilevers, cantilevers with dimples, cantilever with antistiction tips, and doubly clamped microbeams, as shown in Figure 2.21 [101]. The dimples on cantilevers decrease the capillary pull-down force as the surface adhesion energy is proportional to the area [101]; the antistiction tips on cantilevers reduced the area of contact between the structures and the substrate [105], resulting in a decreased adhesion energy at the microbeam tip; the
doubly clamped microbeams increase anchor region strength and decreased contact area between the microbeams and the substrate.

Figure 2.21 Different test structures used to investigate drying of microbeams. (a) regular polysilicon cantilever; (b) cantilever with dimples; (c) cantilever with antistiction tip [105]; (d) doubly clamped beam. Image taken from [101].

However, for PS micromachining, the fabrication of dimples or antistiction tips on microbeams requires complex photolithography or would induce non-uniform porosity in the dimple or antistiction tip region. Such non-uniform porosity would affect properties such as Young’s modulus, residual stress and refractive index, all critical parameters for optical-MEMS based sensors. Furthermore, test results have shown that though dimples and antistiction tips can increase the beam yield when the evaporation method is used, they do not play a significant role for sublimation and supercritical drying methods [101]. Therefore, only cantilevers as shown in Figure 2.21(a) and doubly clamped microbeams as shown in Figure 2.21(d) were designed and fabricated with PS in this work.
2.5 SUMMARY

Conventional micromachining processes for non-porous (bulk) material such as Si were introduced, the patterning with standard photolithography and etching were presented, followed by surface micromachining for release of microstructures.

A detailed investigation of micromachining processes for PS has been carried out. Multistep PS micromachining processes, which aim to provide a pathway for compatibility with CMOS techniques, were established to fabricate released microstructures with laterally uniform porosity, as shown in Figure 2.22.

Figure 2.22 Micromachining processes for released PS-MEMS structures fabrication.
Annealing of PS films under N₂ at 600 °C is critical for creating a passivation layer, which prevents it from being attacked by standard alkaline (KMAH) developer, making it compatible with standard photolithography processes. A pre-photolithographic technique using SOG has been proposed to fill the pores of the PS film, which prevents photoresist seepage into pores, enabling PS microstructures fabrication with relatively thick PS films up to 2.5 μm. This technique significantly improves the applicability of PS film in scalable, complex MEMS fabrication.

Conductive and insulating masks are both applicable for achieving repeated patterning on PS structures. However, they have different characteristics which affect their applicability. Conductive metal masks can form good quality structures with steep sidewalls, but they are only suitable for applications that do not require the subsequent removal of the metal layer, and are not recommended for electropolishing processes. On the other hand, insulating masks can use a wide array of materials, but the mask formation and removal processes can be complex.

Due to its ability to integrate well with the PS anodization process, electropolishing is a promising technique for releasing PS structures. It allows released gaps to be controlled simply by adjusting the current on time. While photoresist masks are typically not suitable for long immersion in HF solution, with process modification including long bakes, thinning and double spins, robust films that can survive electropolishing conditions can be achieved. The use of robust photoresist masks, combined with a critical point drying process are needed to accomplish high yield release of PS micromachined devices. As mask designs (areas) and mask materials change, the applied current needs to be adjusted to achieve electropolishing.

This work presents a thorough investigation of the different processes in completing the PS-MEMS fabrication process, optimising techniques at each stage of process to provide a platform for scalable, complex micromachining based on PS films.
CHAPTER 3
CHARACTERISATION TECHNIQUES FOR POROUS SILICON

In this chapter, various techniques for characterisation of PS films and PS-MEMS structures are presented and discussed. X-ray diffraction and optical profilometry were used to study PS residual film stress, through measuring lattice mismatch and radius of curvature, respectively. The surface profile of PS films and microstructures, and post-electropolishing profile, were investigated using optical profilometry or scanning electron microscopy (SEM). The refractive index, porosity and thickness of PS films were studied by using reflectance spectroscopy modelling. In addition, chemical composition of the PS films after different treatments was studied using Fourier transform infrared spectroscopy (FTIR).

Evaluation of the fabrication processes developed for PS microstructures necessitates the characterisation of the resulting PS-MEMS structures. Various techniques were employed in this work to characterise the mechanical, optical and chemical properties of PS films and/or microstructures, to better understand the PS micromachining. These techniques provide methods in adjusting PS micromachining processes and evaluating the PS microstructures.

3.1 RESIDUAL STRESS MEASUREMENT OF POROUS SILICON FILMS

As discussed in Section 1.2.2, the residual stress in PS plays a significant role in the performance of the microstructures. PS is reported to be a monolithic single crystal but with certain lattice planes misoriented with respect to those of the Si substrate [106],
which will result in a lattice parameter difference (lattice mismatch) between the PS layer and the silicon substrate. For (100) oriented p-type Si the measured lattice parameter is \(a_0=5.4306 \text{ Å}\), and the relaxed lattice parameter of an isolated PS sample (30 \(\mu\text{m}\) thick, 54\% porosity) will present a lattice difference of \(\Delta a=2.3\times10^{-3} \text{ Å}\) [107]. A schematic representation of the PS skeleton is as shown in Figure 3.1, which illustrates the effect of lattice mismatch between the PS film and Si substrate. This lattice mismatch is expected to introduce a compressive stress in the as-fabricated PS film, which can affect the integration of PS devices with integrated circuits based on Si [108]. The stress in PS film has also been observed to change with annealing temperature [109]. Therefore, it is critical to understand the internal stress and stress evolution during the PS-MEMS fabrication processes. Detailed investigations will be presented in Chapter 4 and the main techniques utilised for those investigations are discussed here.

![Figure 3.1 Schematic representation of a cross-section of the silicon structural framework making up the PS layer, and the distortion of the Si crystalline lattice at the PS/Si interface (inset). Image taken from [108].](image)

### 3.1.1 X-ray diffraction measurement

The X-ray diffraction (XRD) rocking curve method is often utilised for thin films to acquire diffraction peaks of the substrate and the overlying thin layer(s). In this work it was employed for measurement of PS layers on Si substrate [110]. The lattice mismatch between PS and Si can be obtained from an analysis of the diffraction peaks, and subsequently the PS film internal stress can be determined based on the lattice mismatch [107]. A Panalytical Empyrean X-ray diffraction system was used to perform rocking curve measurements of the (400) reflection from the lattice plane parallel to the
(100) silicon surface, with a hybrid monochromator and a PIXcel$^{3D}$ detector with fixed anti-scatter slit, employing Cu Kα$_1$ radiation ($\lambda$=1.54052 Å).

The working principle of XRD rocking curve measurements is schematically demonstrated in Figure 3.2. The sample, fixed to a 5-axis stage, is rotated about the omega ($\omega$) axis, to vary the incident angle and produce a rocking curve (intensity versus $\omega$). All 2Theta ($2\theta$) Bragg diffraction angles (including diffraction angles of the film and the substrate) are measured through rotation of the detector over a given range, so that the diffraction angles of both the substrate and the thin layer can be acquired. The incident and reflected angles are set to a value that corresponds to a strong reflection, then scanned through the reflection at very small steps ($\sim 1.7 \times 10^{-6}$ rad), to measure the change of diffracted intensity with angle. A plot is then generated of scattered X-ray intensity ($I$) versus incident related angle ($\omega$).

![Figure 3.2](image.png)

**Figure 3.2** A schematic demonstration of the working principle of X-ray diffraction rocking curve measurements.

For PS samples, the XRD rocking curve measurement provides two Bragg diffraction peaks: one produced by the PS layer and the other from the Si substrate. The separation between the peaks is related to the lattice parameter differences between the PS and the Si. A typical XRD rocking curve for a PS film is shown in Figure 3.3.
Figure 3.3 Typical X-Ray diffraction rocking cure measurement of PS sample on Si substrate.

From XRD measurements, the lattice mismatch can be acquired according to equation:

\[ \frac{\Delta a}{a} = \frac{\Delta \omega}{\tan \omega} \]  

Equation 3-1

where \( \omega \) is the Bragg diffraction peak of Si, and \( \Delta \omega \) is the peak separation between the PS and the silicon. Based on the lattice mismatch between the PS film layer and Si substrate, the average internal stress of each PS film can be calculated as shown in [107]:

\[ \sigma_{ps} = \frac{E_{ps}}{(1+\nu_{ps})} \cdot \frac{\Delta a}{a} \]  

Equation 3-2

where \( \Delta a/a \) is the lattice mismatch between the PS layer and the Si substrate, \( E_{ps} \) is the Young’s modulus of the PS, and \( \nu_{ps} \) is the Poisson’s ratio of the PS, which is assumed to be a constant (\( \nu_{ps} = 0.09 \)) for the PS samples used in this work [107, 111]. The Young’s modulus of PS \( (E_{ps}) \) is known to depend on film porosity \( P \) and is given by \( E_{ps} = E_{Si} (1-P)^2 \), where \( E_{Si} \) is the Young’s modulus of the Si substrate (163 GPa) [4]. Therefore, by using the angle at peak intensity and angle separation between the two peaks, the average internal stress of each PS film was calculated.

However, for samples annealed at high temperature, lateral non-uniform lattice expansion and vertical porosity gradient of PS cause a rapid loss of the PS peak in the XRD measurements, resulting in complete suppression of the PS peak at annealing.
temperatures higher than 320 °C. This effect renders the XRD method unsuitable to provide lattice mismatch information for high temperature annealed samples. Therefore another method is needed to study stress of high temperature annealed PS.

3.1.2 Radius of curvature measurement

Radius of curvature ($R$) is an important mechanical characteristic of MEMS structures [112] and can also be used to quantify the film stress when using Stoney’s equation [113]. This technique is based on measuring the change of the radius of curvature before ($R_1$) and after ($R_2$) formation/deposition of a film on a substrate. For uniform films, the radius of curvature is the radius of the sphere that mathematically best fits the curve in the surface topography.

According to Stoney’s equation, the stress of a PS film deposited on Si substrate can be expressed by the following equation:

$$\sigma_{ps} = \frac{E_{si}}{6(1-v_{si})} \frac{t_{si}^2}{t_{ps}} \Delta \left( \frac{1}{R_1} - \frac{1}{R_2} \right)$$  \hspace{1cm} \text{Equation 3-3}

where $E_{si}$ is the bulk Young’s modulus of the Si substrate, and $v_{si}$ is its Poisson’s ratio ($v_{si} = 0.26$). $t_{si}$ and $t_{ps}$ are thickness of the Si and PS layers, which are 280±25 µm and 2.5±0.1 µm respectively in the experiments presented in this work. The radii of curvature for the Si substrate before and after formation of the PS layer are the key measurement parameters that relate to the stress. Importantly, by measuring the radius of curvature of the same sample with and without the PS film, via optical profilometry measurements of the surface, high accuracy (differential) stress measurements can be obtained.

Optical profilometry is a non-contact method to acquire surface morphology information from samples, which uses the reflected light from the sample and interferometer to determine the characteristics including surface topology, roughness, radius of curvature and film thickness. In this work, the radius of curvature of the PS samples was studied utilising a Zygo NewView™ 6000 optical profilometer with a white light filter based on a centre wavelength of 550 nm and bandwidth of 125 nm, and employed the instrument software feature allowing separate measurements to be
stitched together to acquire a large area profile of the sample. This technique enabled measurement and analysis of a surface area much larger than that available with a single measurement. It increased the field of view without compromising lateral or vertical resolution, allowing a profile of the entire sample area to be acquired and analysed.

In this work, the radius of curvature was measured by profilometer on the polished backside of the silicon wafer. The measurement on the backside avoided any optical interference that may have resulted from the low refractive index, optically transparent thin PS film. To accurately measure the change of radius of curvature, the PS sample was firstly cut into a rectangular shape (~3×15 mm²) after fabrication, because the curvature of a sample having this shape is constant over the sample surface and proportional to the thin film stress [114]. Subsequently two spots were marked along the length of the backside (Si side) of the sample. A stitch measurement was carried out with the profilometer between the two marked spots to acquire the radius of curvature over a spatial range of approximately 13 mm, as shown in Figure 3.4. Then the sample was dipped in a 5% (w/w) KOH solution for approximately 15 s to remove the PS layer, and the radius of curvature was measured again, between the same marked spots. This allowed the difference of radius of curvature (Δ(1/R) = 1/R₁ - 1/R₂) with and without the PS film to be acquired.

![Figure 3.4](image)

*Figure 3.4 Example of profilometer measured height profile of backside (Si side) of a rectangular PS sample.*

The marked spots were used as a reference to make the measurements in the same region before and after removal of PS. This minimises the Se due to surface curvature variation across the wafer. The curvature change of a bare Si substrate after a 5% KOH
dip for 15 s was also tested, and was found to introduce <7% uncertainty to the PS film stress.

The radius of curvature measurement method is useful for investigating the evolution of PS film stress after the films have been exposed to different thermal and chemical processes. However, since it necessitates the removal of the PS film during the measurement, this method is destructive. As such, for ageing (oxidation) effect studies of a particular PS film, this method is not preferred compared to the lattice mismatch measurement via XRD.

### 3.2 SURFACE MORPHOLOGY

Surface profile is an important factor while studying the PS-MEMS structures, and various tools can be used to acquire detailed information including surface morphology, thickness, roughness and curvature.

Surface profilers and scanning probe microscopes (SPM) are conventional surface topography apparatuses that employ a stylus or cantilever with tip to probe sample surface and determine height variation during measurement. A Dektak 150 surface profiler (Veeco Instruments Inc.) was employed in this work to acquire height differences between different layers including photoresist, metal and Si substrate. However, due to the porous structure and low Young’s modulus of PS, the physical contact between stylus and PS film results in damage to the sample, as shown in Figure 3.5. As can be seen in the image, after a linear scan was carried out across the top of the PS film, a permanent groove was left in the sample, which would affect the porosity uniformity or even cause failure of the microstructure if such profiling was implemented on PS-MEMS devices.
3.2.1 Optical profilometry

Compared to the use of a profiler and SPM, optical profilometry is a non-contact technique, avoiding damage to the sample. This advantage makes optical profilometry particularly useful for the measurement of PS films due to the extremely low Young’s modulus of the films.

A film analysis application incorporated in the Zygo NewView™ 6000 optical profilometer was utilised for the optical profilometry in this work. It was carried out by a special functional data analysis (FDA) module to identify the substrate and film surfaces, then provide information including film thickness, surface topography and roughness of top layer, lower layer and the substrate. This technique is essential when using optical profilometry for low refractive index (for PS, \(n=1.3\sim1.8\)) transparent films.

Using the film analysis provided by the profilometer, a variety of interesting characteristics of released PS structures can be acquired, including surface topography, PS film thickness, roughness of suspended PS layer and Si substrate surface profile. The analysis software provides a 3D model of the PS-MEMS structure based on the measurement, as shown in Figure 3.6. In this work, the profilometer was also utilised to measure curvature/deflection of PS microbeams in order to assess structural (including stress) changes due to processing or sensing, which will be detailed in Section 6.1 and Section 6.4.2.
3.2.2 Scanning electron microscopy

Scanning electron microscopy (SEM), which scans an electron beam across the area of interest, is typically utilised to acquire much higher resolution images compared to optical profilometry or optical microscopy. In this work, SEM was used on PS-MEMS structures to provide morphology information through plane view imaging and morphology and layer information from cross-sectional view imaging.

It is common practice to use a thin conductive coating on semiconducting materials for optimal imaging in SEM, because the conductive coating could increase the electrical conductivity and therefore the quality of the SEM image. However, even a 1 nm thick Pt coating can introduce distortion of the morphology and resulting misleading interpretation of the images [45]. To avoid this effect, SEM measurements in this work were carried out with uncoated PS samples. Example cross-sectional SEM images of a PS film after formation and after N\textsubscript{2} annealing are shown in Figure 3.7(a)-(b).

![Figure 3.7](image)

**Figure 3.7** Typical cross-sectional SEM images of the PS fabricated in this work (beam voltage of 1 kV). (a) PS after formation; (b) PS after N\textsubscript{2} annealing.
SEM tools used in this work include a Zeiss 1555 VP-FESEM, a TESCAN VEGA SEM and a Hitachi Benchtop SEM TM3030. The actual accelerating voltage used for each SEM instrument varied from 0.5 kV to 15 kV, due to different configurations and charging effects in each apparatus. However, to avoid over charging that degrades SEM image quality, low accelerating voltage (<5 kV) was preferred during the measurements.

3.3 PHYSICAL AND CHEMICAL CHARACTERISATION OF PS FILMS

3.3.1 Porosity and refractive index

Typical methods of porosity determination include direct measurement through gravimetry [115] and indirect measurements such as those based on reflectance spectrum measurements [116]. The gravimetry method is straightforward but destructive, while the reflectance spectrum method is non-destructive but needs a model to extract the physical properties from optical measurements [40]. Importantly, the modelling of the measured spectrum allows sufficient flexibility for estimation of porosity gradient. Gravimetry measurements must assume a uniform porosity and hence can only provide an “average” porosity.

Since fabricating uniform porosity PS microstructures is one of the goals in this work, the porosity gradient is an important property to investigate. In addition, multiple measurements on the same sample are necessary to study the effects of different fabrication processes on PS. Therefore, as a non-destructive method which can estimate the porosity gradient, the reflectance spectrum measurement was utilised in this work. When the reflectance spectrum method is used for thin film measurements, the optical path length, and therefore the refractive index, can be extracted due to the multiple reflected beams from the various interfaces. In the case of PS thin films, the relevant interfaces are air/PS and PS/Si. Once the refractive index has been determined, a model is required to relate that to the porosity. The models applicable to extraction of porosity from optical data obtained by the reflectance spectrum method include the Bruggeman effective medium approximation [117], Maxwell-Garnett theory [118] and Volume Averaging Theory [119, 120].
In this work, based on the PS film type (meso-porous) under investigation, the Bruggeman effective medium approximation was considered as the most suitable model [45, 121] to estimate porosity, film thickness, refractive index and porosity gradient of the PS films. Through a differential evolutionary algorithm as developed by M. Wormington et al. [122], the measured reflectance spectra of PS films were auto-fitted and parameters extracted from the fit data [45], as shown in Figure 3.8. The investigation of the relationship between PS formation conditions (such as HF concentration, anodisation current density) and these film properties is a necessary foundation to build PS microstructures with particular film requirements.

Figure 3.8  An example for reflectance spectrum measurement result of PS film, and parameters extracted from the fit data based on Bruggeman effective medium approximation.

3.3.2 Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) is a technique generally utilised to obtain an infrared spectrum of absorption, emission or photoconductivity of a target sample, such as solid, liquid or gas. A FTIR spectrometer can collect high spectral
resolution data over a wide spectral range simultaneously, and provide chemical composition information of a sample.

In this work, since the Si substrates used for PS formation were moderately doped with resistivity of 0.09±0.02 $\Omega$ cm (equivalent doping density of $2.4\times10^{17}$ cm$^{-3}$, low loss in the infrared) and double side polished, transmissive FTIR was suitable to obtain an infrared absorption spectrum of the PS film. However, the absorption spectrum includes chemical signatures not only of the PS film, but also of the silicon substrate and resonances from the front and backside of silicon [45]. To remove these signatures, an untreated silicon wafer was used for the background measurement that is always taken to normalise the spectrum, to exclude the influence of the silicon substrate. In this work, all the transmissive FTIR measurements were undertaken with a Perkin-Elmer Spectrum One FTIR spectrometer, to obtain absorption spectra from 600 cm$^{-1}$ to 2600 cm$^{-1}$, with spectral resolution of 4 cm$^{-1}$.

3.4 PS MICROBEAM CHARACTERISATION TECHNIQUES

As typical MEMS structures, microbeams (cantilevers and doubly clamped microbeams) were fabricated in this work for investigation. Therefore, suitable techniques are required to characterise those beams.

Two major read-out methods, static mode (typically detection of the height change) and dynamic mode (typically detection of motion/resonance), are employed in characterising MEMS structures. The static mode is utilised with optical techniques which are able to achieve extremely high precision sensitivity. Examples are the optical filter in Figure 1.1 and the sensing investigation which will be discussed in Section 6.4.1. In this work, the height change of microbeams was measured using the non-contact optical profilometry technique as discussed in 3.2.1.
However, the optical techniques are limited with respect to the number of MEMS devices they can address simultaneously [36], especially for application to measurement of a scalable technology which could contain thousands of microstructures in one single chip. In contrast, the dynamic mode based on electronic interrogation techniques is able to simultaneously address multiple microstructure measurements, which is cost effective [36]. This method provides a path to scalable sensing device production and application, and has been used for released PS microbeam vibration detection in this work.

The laser Doppler vibrometer system utilised in this work is schematically represented in Figure 3.9. The sample was actuated through a piezoelectric element driven by a function generator (Agilent 33220A). The function generator was controlled through a Labview programme to carry out a sweep over a selected frequency range using a sine wave signal to actuate the sample. The output of the laser Doppler vibrometer controller (Polytec OFV-5000) was measured on a digital oscilloscope (Rigol DSO 5014A). During the measurements, the sample was kept in a vacuum chamber which was maintained at a pressure of below $6.0 \times 10^{-3}$ Torr. The vacuum environment was important to eliminate the effect of squeezed film damping [123] which can suppress the resonance of the vibrating beam.

![Figure 3.9 Schematic of laser Doppler vibrometer system for resonant frequency measurement of the PS microbeams.](image_url)
The laser Doppler vibrometer utilised a differential fibre probe, launched through a microscope onto the sample. The reference beam of the laser Doppler vibrometer was reflected off the silicon substrate while the measurement beam was reflected off the PS microbeam. This ensured that the measured signal from the vibrometer was due only to the microbeam displacement induced by the piezoelectric actuator and did not arise from other sources. Both velocity and displacement of the microbeam can be measured in real-time through the vibrometer controller, which was equipped with different decoders with specifications as shown in Table 3-1. A real-time image of the sample could be imaged by a digital camera connected to the microscope, which helped adjust the position of each laser beam of the differential laser Doppler vibrometer.

<table>
<thead>
<tr>
<th>Decoder</th>
<th>Type</th>
<th>Best resolution</th>
<th>Frequency bandwidth</th>
</tr>
</thead>
<tbody>
<tr>
<td>VD-02</td>
<td>Velocity, analog</td>
<td>0.15 µm/s</td>
<td>0.5 Hz - 1.5 MHz</td>
</tr>
<tr>
<td>VD-06</td>
<td>Velocity, digital</td>
<td>0.5 m/s</td>
<td>0 Hz – 350 kHz</td>
</tr>
<tr>
<td>DD-500</td>
<td>Displacement, digital</td>
<td>15 pm</td>
<td>0 Hz - 250 kHz</td>
</tr>
</tbody>
</table>

Table 3-1 Decoders available for differential laser Doppler vibrometer measurement.

Through the vibrometer measurement along with sweep over a selected frequency range, resonant peaks can be acquired as shown in Figure 3.10. The frequency corresponding to the highest resonant peak in the measurement is the fundamental mode of the microbeam resonance.
3.5 SUMMARY

In this chapter a series of characterisation techniques were discussed in relation to their application to characterise PS films and PS-MEMS structures.

X-ray diffraction and optical profilometry are both suitable to study residual stress in PS films. However, both techniques have advantages and limitations. For samples annealed at temperatures higher than 320 °C, non-uniform lattice expansion/porosity resulted in the complete loss of the PS peak in the XRD measurements. A radius of curvature measurement based on optical profilometry is suitable for high temperature annealed PS film stress analysis, but it is necessary to etch away the PS film, which renders it impossible to repeat measurements or perform subsequent steps on the same sample.

Surface morphology of PS-MEMS structures can be investigated by physical contact measurement with a surface profiler, optical profilometry or SEM. The profiler is suitable for height difference measurement of different layers, but it will induce damage on the PS film due to the stylus contact. Optical profilometry and SEM can provide surface information on different scales. Optical profilometry typically allows vertical scan resolution of <0.1 nm, and lateral resolution on the order of 1 µm. SEM can
achieve sub-nanometer beam resolution even at high beam voltage (20 kV), providing a technique for high resolution measurement of the PS film and PS-MEMS structures.

PS film porosity, thickness, refractive index and porosity gradient can be extracted based on the Bruggeman effective medium approximation model applied to reflectance spectrum measurements. The chemical composition of the PS film after different treatments can be acquired by transmissive FTIR absorption spectrum.

For characterisation of PS microbeams, static mode and dynamic mode are typically utilised. Static mode with optical measurement of microbeam height change can be carried out through profilometry. Dynamic mode with vibration measurement can be implemented through Doppler vibrometer to identify the fundamental resonant frequency of fabricated PS microbeams.

Through the discussion above, techniques/tools have been developed or adapted so that all necessary information to evaluate and optimise the micromachining processes and subsequent micromachined structures could be obtained, leading to the successful PS-MEMS structures developed in this work.
CHAPTER 4
RESIDUAL STRESS IN POROUS SILICON FILMS

In this chapter, stress in PS films was studied based on lattice mismatch and radius of curvature measurements. The relationships between porosity, annealing temperature, oxidation and stress were investigated using the lattice mismatch (XRD) measurements. In addition, the stress change for high temperature (>320 °C) annealed PS films, which could not be measured via XRD, was assessed by curvature based measurements. The internal stress of PS at different stages of MEMS processing was subsequently determined to understand the implications of processing steps on the stress as well as potential methods to control or modify the stress.

Residual stress in MEMS devices is extremely important and has been a significant focus of these investigations, because it dramatically affects the mechanical properties of MEMS devices due to the small dimensions of the devices.

In particular, the effect of stress on PS-MEMS structures is more significant than on equivalent bulk material MEMS structures due to the very low Young’s modulus of the PS film. Furthermore, PS-MEMS fabrication requires PS to be subject to a series of physical and chemical treatments, which can cause structural changes in the PS film and significant stress evolution. As a result, unfavourable effects including deformation, fracture, delamination and excessive structural changes are introduced if the residual stress is not well controlled, resulting in low process yield, breakage, or even failure. Though internal stress evolution in PS films under different treatments during the fabrication process is essential to understand, no thorough investigation has been reported to date. Therefore, to utilise PS as a support material in micromachining process, the residual stress in film must be investigated and controlled.
4.1 FACTORS AFFECTING PS FILM STRESS

PS-MEMS fabrication requires PS films of different properties (particularly porosity) depending on the application. In addition, the PS films are required to go through a series of chemical and physical processes which can affect the optical, thermal, electrical and/or mechanical properties of the as-fabricated film. Specifically, these processes are likely to induce changes in PS film stress. Furthermore, the effect on mechanical characterisations of oxidation under ambient conditions is unclear. Therefore it is necessary to investigate effects of common treatments during MEMS processes on PS film stress.

Factors including porosity, oxidation, annealing conditions (temperature, ambient, duration and flow rate) and HF immersion are critical in affecting film stress through the PS film formation and microstructures fabrication processes. For the PS film stress study in this work, different treatments have been applied to the films. The PS film formation and annealing processes were implemented following the processes as discussed in Section 2.3.1. After fabrication of the PS films, the samples employed for the annealing investigation were annealed under either vacuum or N₂ at atmospheric pressure at different temperatures. Subsequently, to study the effect of HF immersion, selected annealed PS films were dipped in a 10% HF/ethanol solution for at least 15 s, which removed the oxide and returned the film surface to a Si-H/Si-H₂ state.

In this work, both XRD rocking curve and radius of curvature measurements as discussed in Section 3.1 were employed to study the factors affecting PS film stress.

4.1.1 Relationship between PS film stress and porosity

Porosity of PS is a common physical factor that can be easily adjusted by changing the concentration of HF solution and/or current density during anodisation process. Various properties of PS including refractive index, Young’s modulus, surface area and density are determined by porosity.

Rocking curve diffraction patterns for as-fabricated PS layers of different porosity are shown in Figure 4.1. With an increase of PS film porosity from 71% to 87%, the PS peak moved further away from the silicon substrate peak, which is consistent with
previous studies [124]. Based on the lattice mismatch between the PS film layer and silicon substrate, the average internal stress of each PS film could be calculated [107].

Figure 4.1 X-ray rocking curve diffraction patterns for as-fabricated PS layers of different porosity (P).

The measured stress ($\sigma$) along with the Young’s modulus ($E_{\mu}$) is plotted in Figure 4.2(a) as a function of porosity, indicating that the internal stress of PS changed from -7.93 MPa ($P=71\%$) to -0.79 MPa ($P=87\%$) over the porosity range studied, where the negative sign of stress indicates it was compressive in all as-fabricated PS. A 23% change in porosity accounted for a change in the internal stress of nearly 90%. Hence porosity variation achieved by changing anodisation current density during fabrication is a simple method to tailor the stress in these films. The ratio of stress versus Young’s modulus of PS along with porosity is plotted in Figure 4.2(b). It is shown that the ratio is relatively constant (between $2\times10^3 :1$ and $2.25\times10^3 :1$) over this porosity range, which indicates that the porosity of PS is a key factor in determining both film stress and Young’s modulus, and the two mechanical properties have similar trends with the change of porosity.
4.1.2 Ageing and ambient oxidation effects on stress

As is well known in PS research, ageing (oxidation) in an ambient environment is a factor that will cause significant change in chemical property, porosity and thickness of the film. No systematic investigation has been undertaken on the effect of oxidation on PS film stress during the ageing process. But this effect is critical to understand due to its close relationship with mechanical properties and stability in MEMS structures. The XRD measurements of PS film after fabrication and 300 °C annealing for 6 minutes are shown in Figure 4.3(a)-(b). The samples for this investigation were fabricated to form PS layers with a porosity $P=81\pm1\%$ and physical thickness $t=2.5\pm0.1\,\mu\text{m}$. The XRD measurements showed...
measurements of PS film after fabrication and 300 °C annealing for 6 minutes are shown in Figure 4.3(a)-(b). After significant time exposed to air (approximate temperature of 21 °C and humidity of 35%), both the samples showed a significant change in stress as a result of oxidation.

In Figure 4.3 (a), the PS peak of the aged as-fabricated PS sample moved further away from the silicon peak, indicating an increase in compressive stress. In Figure 4.3 (b), the PS film showed an initial tensile stress after annealing at 300 °C. This effect will be discussed further in the next section (Section 4.2) as part of a more detailed investigation into annealing effects on stress. However, of interest here is that the stress became compressive after one week of exposure to air, with the compressive stress
subsequently increasing significantly with time. The decrease of the PS peak intensity with increased exposure duration is most likely due to the oxidation, which results in lattice distortion and greater non-uniformity in the expansion of the film [125].

PS annealed under N₂ at 600 °C for 6 minutes has shown the nitridation of PS and reduction of effect of oxidation in air (normal ambient, meaning at or around standard ambient temperature and pressure), providing a path for the films to be stable in air and compatible with standard photolithography [45]. The stress evolution of this annealed PS film in air is critical to understand for utilisation in MEMS. To carry out long term ageing tests, a 2.5 µm thick PS sample was firstly annealed under N₂ at 600 °C for 6min, then exposed to atmospheric ambient (approximate temperature of 21 °C and humidity of 35%) and measured at different times, using radius of curvature measurements. The stress evolution of the passivated PS film exposed in air is shown in Figure 4.4. A slight reduction of tensile stress is observed along with exposure time in air, indicating the film stress was slightly oxidised. But a 60-day exposure had little effect on the stress, which is consistent with previous measurements on similarly annealed material which showed a refractive index change of less than 1% over the same period as shown in Figure 4.5 [45].

![Figure 4.4 The stress evolution with time exposed to air for 2.5 µm thick PS sample annealed under N₂ at 600 °C for 6 min.](image-url)
It is worth noting that the investigation was carried out using radius of curvature measurements, which is a destructive method as discussed in Section 3.1.2. Therefore, though samples for each measurement were from the same annealed PS film, they were cleaved from different regions of the wafer. As a result, any spatial variation of porosity and thickness may affect the variability of the stress measurements.

![Graph showing change of refractive index with time exposed in air for PS sample annealed under N₂ at 600 °C for 6 min.](image)

*Figure 4.5 Change of refractive index with time exposed in air for PS sample annealed under N₂ at 600 °C for 6 min. Data adapted from [45].*

### 4.1.3 Modification of stress by HF immersion

In any MEMS fabrication process that involves PS, both annealing and anodisation/electropolishing will conventionally be applied, the latter of which requires samples to be immersed in HF solution. Therefore it is important to investigate the effect of HF immersion on PS film stress. Subsequently some samples were immediately annealed in N₂ atmosphere for 6 min at different temperatures. Selected samples annealed at 300 °C were dipped in a 10% HF/ethanol solution for 15 s, to remove any surface oxide and re-terminate the film surface with H-bonds.

XRD rocking curve measurements at each stage of the test were obtained as shown in Figure 4.6. After annealing, the PS Bragg peak shifted away from its original position. Moreover, the peak for the sample annealed at 300 °C moved to the right of the Si peak, indicating the film became tensile as predicted by previous results [126]. However, the
peak moved back to within $3 \times 10^{-3}$ degrees of the original peak after the HF dip. Through calculations as discussed in Section 3.1.1, it was found that the internal stress of the PS changed from -2.0 MPa to 1.2 MPa (tensile) after annealing at 300 °C, and back to -1.9 MPa after the HF dip. This trend is consistent with previous reports of vacuum annealing and the effect of a HF dip on PS, attributed to surface hydrogen desorption and re-adsorption, respectively [127, 128]. These results show both annealing and the HF dip will modify the stress, so that any process combining both will result in a wide stress range with the film.

![Figure 4.6 XRD measurements showing stress after various process steps: (a) after fabrication; (b) after annealing at 250 °C; (c) after annealing at 300 °C; (d) after HF dip of 300 °C annealed sample.](image)

In Figure 4.6 (and previously in Figure 4.3), the low intensity and large full width at half-maximum (FWHM) of the PS peaks are most likely affected by the porosity gradient inside the film and degraded crystalline quality by surface oxidation [125]. The porosity gradient causes non-uniform lattice expansion during annealing, further decreasing the PS diffraction peak intensity. After the HF dip, it can be seen in Figure 4.6 that in addition to the change in position, the PS diffraction peak intensity has also been increased closer to the original intensity of the as-fabricated film. Again, this is likely due to the restoration of H-bond surface termination after the HF dip.
4.2 STRESS EVOLUTION WITH ANNEALING AND PASSIVATION

Annealing of PS under various ambient conditions to form a passivation layer on the film have been widely used to adjust its physical or chemical properties [39, 129], including photoluminescence and chemical resistance. However, these processes are likely to induce changes in PS film stress, as indicated by the results in Section 4.1.

Previous PS film stress studies focused on either in situ ultrahigh vacuum (UHV) [128] or treatment in N\textsubscript{2} below 350 °C [130, 131], and thus did not investigate how PS stress evolves in non-vacuum temperatures higher than 475 °C [132] for which continued hydrogen desorption occurs. Though the temperature dependence of PS stress and its relationship with hydrogen desorption have been reported [133, 134], changes in stress after relatively high temperature annealing in N\textsubscript{2} or after repeated HF exposure, as would be common in a multistep PS-MEMS fabrication process, have not been investigated. Thus the extent of stress changes after typical annealing under different ambient conditions must be determined.

4.2.1 Nitrogen annealing

N\textsubscript{2} ambient annealing of PS has shown excellent standard photolithography process compatibility [49] and stability in air as discussed in Chapter 2 and reiterated in Section 4.1.2. Therefore, the effect of this annealing process on PS stress is essential to understand and hence will be the first condition to evaluate.

The stress (σ) measured by both lattice mismatch and radius of curvature (R) based methods are shown in Figure 4.7, as a function of annealing temperature (T). The two methods are in good agreement for stress measurements at low temperatures (<350 °C). However, as outlined in Section 3.1, only the radius of curvature based method can reveal how the stress changes for PS films annealed at high temperatures.
Chapter 4

Figure 4.7  PS stress as a function of annealing temperature, measured via lattice mismatch and radius of curvature (R).

The evolution of stress with temperature is extremely complicated and depends strongly on the ambient annealing condition and whether the measurements are conducted *in situ* or after annealing.

To aid in this understanding, four regions of interest are identified in the stress induced thermal annealing data shown in Figure 4.8(a). Thermal desorption of hydrogen from porous silicon is well known and has previously been measured by Gupta *et al.* [8] and is shown for comparison in Figure 4.8(b). The data shows two peaks in the desorption of hydrogen with increase of annealing temperature, starting at ~350 °C. However the data in Figure 4.8(b) was measured *in situ* under high vacuum, which is typical of thermal desorption spectroscopy (TDS) measurements.
In region A, no adsorption occurs within the films so that the stress remains unchanged. In region B, no significant hydrogen desorption has occurred, suggesting that only the N\textsubscript{2} within the pores is altering the stress. Previous measurements of stress in vacuum have observed no tensile stress increase in the temperature range of region B [128] while other reports of films annealed in N\textsubscript{2} have measured an increase in tensile stress [130, 131], supporting the contention that the presence of N\textsubscript{2} plays a role in this region. In region C, significant dihydride desorption occurs from the pore walls, so that upon removal from the thermal annealer to undertake measurements (as was implemented here), oxidation occurs which increases the compressive stress. Beyond 500 °C in region D, the desorption of monohydride species and the passivation layer formed in the
presence of the N\textsubscript{2} which have previously been reported [39] results in a return to tensile stress that is stable once removed from the thermal annealer (no oxidation occurs).

As a result of the competing oxidation and nitridation processes this stress evolution of N\textsubscript{2} annealed PS films is different from that of vacuum annealed samples measured \textit{in situ} [128], which show a continuous increase of tensile stress with annealing temperature.

The evolution of the chemical state of the surface during the above process was investigated by FTIR, as shown in Figure 4.9. When the annealing temperature was below 350 °C, the spectra were similar to that for as-fabricated PS, with typical Si-H\textsubscript{x} stretching modes at 2089 cm\textsuperscript{-1}, 2113 cm\textsuperscript{-1}, 2129 cm\textsuperscript{-1}, Si-O-Si resonance at 1102 cm\textsuperscript{-1} corresponding to residual oxygen impurities in Cz grown silicon wafers [135], and a Si-H\textsubscript{2} scissor mode at 905 cm\textsuperscript{-1} [136]. When the annealing temperature was increased to 350 °C, the Si-H\textsubscript{2} peak disappeared due to the Si-H\textsubscript{2} desorption. Subsequently a strong Si-O resonance at 1053 cm\textsuperscript{-1} was measured when the annealing temperature reached 475 °C, indicating significant oxidation of the PS surface. Finally, a major N-H peak (1170 cm\textsuperscript{-1}) appeared at 600 °C, along with a reduction in the Si-O resonance, which was due to the nitridation process [137, 138]. This FTIR spectrum evolution is consistent with the hydrogen desorption processes and corresponding mechanism for stress change discussed above.

\textit{Figure 4.9} FTIR spectra of PS films annealed in N\textsubscript{2} at different temperatures.
4.2.2 Interrelated oxidation and nitridation (passivation layer) effects on stress

To further understand the effects of oxidation and nitridation on stress in the annealing process, PS films were annealed for 6 min under vacuum and compared with the previous data (Figure 4.8) obtained under nitrogen (at a flow rate of 1000 sccm) as shown in Figure 4.10. For both sets of data the stress was measured post-annealing, after a short exposure to air. For the vacuum annealed PS, the stress followed a similar trend to the N₂ annealed samples when temperatures were <450 °C, however the magnitude of the stress change observed was significantly lower. As discussed earlier, this is not unexpected due to the enhancement in hydrogen desorption at lower temperature when annealing in N₂. Similarly, at higher temperatures (450 °C < T < 550 °C) both samples exhibit a return to compressive stress as a result of oxidation after removal from the chamber, but with the compressive stress for the N₂ annealed samples peaking around 150 °C less than for vacuum annealing samples. In both cases, the competition between tensile stress from hydrogen desorption and compressive stress from oxidation results in inflection points in the $\sigma$-T data. As temperature increases above 550 °C, however, there commences a difference in trend, rather than just a change in magnitude, between the two annealing sets. While compressive stress continues to dominate the data for the vacuum annealed sample, in N₂, nitridation of the porous surface above 550 °C reduces subsequent oxidation at ambient conditions, and results in a tensile film. Samples annealed for 6 min at 600 °C in N₂, consistent with previous investigations [49], exhibited a tensile stress of 2.0 MPa. Annealing in N₂ at 600 °C for only 5 s resulted in a film stress of -1.6 MPa (compressive), as the annealing time was not long enough to form a significant nitridation layer on top of PS surface. This indicates the importance of the nitridation process at higher than 550 °C in preventing oxidation and achieving a stable tensile stress. As indicated in Figure 4.10 tensile stress has not been observed in films annealed at high temperature in vacuum, as indicated by the data from Buttard et al [128]. Hence the nitrogen, 600 °C, 6 minutes anneal results in a distinctly different, stable stress state in the film.
Figure 4.10  Comparison of PS stress change with annealing temperature under different conditions: (a) Vacuum, in situ measured, 65% porosity, extracted from [128], (b) N₂ (6 minutes, at flow rate of 1000 sccm), measured in air, (c) vacuum (6 minutes), measured in air.

Next, the proposed mechanism was investigated further via HF immersion. During processes to fabricate PS-MEMS structures [139, 140], samples could be often and repeatedly annealed or immersed in HF, which will remove any oxide layer but will also remove the passivation layer from N₂ nitridation and re-terminate the surface with hydrogen, as discussed in Section 4.1.3. Additionally, as repeated multistep micromachining processes are important in fabricating PS-MEMS structures, the effect of alternating oxidation and HF immersion steps on the stress state needs to be understood. Figure 4.11 (a) shows the effect of a short 15 s HF dip after the samples have been annealed in N₂ for 6 min at 1000 sccm. Up to a temperature of 500 °C, the samples remain compressive and return to a state of stress very similar to the initial as-fabricated PS stress state. Given the large change in tensile and compressive stresses observed in these samples prior to the HF dip (Figure 4.10), the return to slightly compressive state after HF immersion offers a simple method to reset the stress.

The highest state of compressive stress after a HF dip was for the sample annealed at 475 °C, which corresponds to the highest compressive stress measured before the HF dip (Figure 4.8, Figure 4.10). This temperature corresponds to the Si-H desorption peak shown in the vacuum hydrogen desorption data in Figure 4.8, leading to significant
Subsequent HF immersion would strip the oxide and increase the effective porosity of the sample. However Figure 4.1 suggests an increased porosity should lead to a drop in stress, not the increase observed in Figure 4.11 (a). At these temperatures it appears a permanent structural change has taken place, which may indicate the onset of sintering. In further support of this is that the HF dip caused only a slight reduction in tensile stress for annealing (nitridation) above 550 °C. For example, the HF dip caused a reduction from 2.0 MPa to 1.3 MPa after 15 s dip for the 600 °C annealed sample, indicating it was not residual oxide on the surface causing the stress. At these annealing temperatures the tensile stress is apparently fixed due to permanent structural changes after annealing.

The final step in investigating the competing nitridation and oxidation effects was to modify the ambient gas during nitridation. Figure 4.11 (b) shows the results for PS films annealed under a mixture of nitrogen/oxygen (N₂/O₂ = 800 sccm/200 sccm). An increase in compressive stress with temperature was observed, indicating once again the effect of oxidation on stress. However, following further treatment of dipping in HF for 15 s, though still compressive, the resulting stress of the PS annealed at different temperatures in N₂/O₂ mixture moved significantly closer to zero-stress (-0.7 MPa for 600 °C annealed sample). This indicates removal of oxide on the surface for PS annealed in N₂/O₂ mixture has occurred, but the structure does not show a permanent change at 600 °C as observed the samples annealed in N₂. The combination of high temperature (600 °C) and a pure N₂ flow is expected to give rise to this structural change, which did not occur under a mixture of nitrogen/oxygen due to an oxide layer preferentially covering the PS surface.
Figure 4.11  PS film stress under different treatment. (a) HF dip effect on N$_2$ annealed PS films. (b) Stress of PS films annealed under mixture of nitrogen and oxygen (N$_2$/O$_2$ = 800 sccm/ 200 sccm), and HF dip effect on annealed film.

Other experiments were undertaken to confirm the role of the 600 °C N$_2$ annealing (passivation) step in achieving stable tensile stress. This included introducing low temperature preheating steps, keeping vacuum conditions during temperature ramping, or other modifications to the standard passivation process. All such annealing modifications resulted in compressive stress either immediately or gradually (<1 week) indicating oxidation. Therefore only a complete passivation of as-fabricated PS will result in subsequent stable tensile stress.
4.3 N\textsubscript{2} ANNEALING CONDITIONS

Annealing temperature has shown a significant impact on PS film stress as discussed in the previous sections. On the other hand, the effects of other important annealing conditions on PS stress have not been investigated before. Therefore, it is necessary to implement a comprehensive study of the relationship between annealing conditions and film stress. Subsequently an optimised annealed technique suitable for PS-MEMS process can be developed.

4.3.1 Annealing duration

The previously discussed optimised technique based on N\textsubscript{2} annealing at 600 °C reduces the effect of oxidation in ambient air, and makes the films compatible with standard photolithography [49]. Previous studies also found that annealing duration is a factor affecting the chemical resistance of the PS film [45, 49]. Therefore, the effect of annealing duration on PS film stress was investigated, to understand if the annealing time had a significant effect on stress as well.

Figure 4.12 shows the residual stress comparison for PS films annealed at 600 °C, with a N\textsubscript{2} flow rate of 1000 sccm, under different durations from 5 s to 48 min. As shown in the figure, annealing in N\textsubscript{2} at 600 °C for only 5 s resulted in a film stress of -1.6 MPa (compressive), as the annealing time was not long enough to form a significant nitridation layer on top of PS surface. However, when annealing duration was above 6 min, the residual stress in PS film tended to be relatively stable tensile stress. Previous studies have reported that annealing in N\textsubscript{2} at 600 °C for 6 min is enough for the PS film to survive in standard TMAH developers for at least 80 s [45]. Discussions in Section 4.1.2 and Section 4.2.2 have shown that this annealing process also enables the PS film to maintain a stable tensile stress through long term exposure to air and HF immersion treatment. Therefore, these annealing conditions result in a PS film that satisfies both chemical resistance and stress requirements for MEMS fabrication, and as a result, were employed through the remainder of this work for PS micromachining.
Figure 4.12  Comparison of PS annealed at 600 °C, under different durations, annealing was undertaken in N₂ at a flow rate of 1000 sccm.

4.3.2 Nitrogen flow rate

N₂ flow rate is another factor that can be adjusted during the annealing process and has been reported to affect the chemical resistance and optical thickness reduction (OTR) after HF immersion [45]. Compared to low flow rate (250 sccm), high flow rate (1000 sccm) results in a film with weaker chemical resistance but less OTR after HF immersion (less oxidation). Therefore modification of flow rate can be applied to tune the properties of the PS. Prior to this work the effect of flow rates on PS film residual stress had not yet been mapped.

Figure 4.13 shows the evolution in stress along with N₂ flow rate at constant pressure of 1 atmosphere. Samples were annealed for 6 min in the annealing chamber as discussed in Section 2.3.1, at the temperatures of 375 °C (peak tensile stress) and 475 °C (peak compressive stress) respectively. As shown in the plot, the residual stress in the PS films tended to increase rapidly with flow rate increase from 20 sccm to 250 sccm. However this trend became less significant when flow rate was above 250 sccm. One possibility is that N₂ flow across the PS surface may result in an enhanced venting effect, compared to a lower pressure above the sample (Bernoulli principle). The pressure differential from inside to outside the PS would drive any species (H₂) out of the sample [45]. With the increase of N₂ flow rate, H₂ is expected to be driven out of PS more
rapidly, allowing the film to perform a more energetic nitridation or oxidation process, which increases the stress in PS film. This passivation effect causes significant stress change at flow rates from 0 to 250 sccm. But for flow rates higher than 250 sccm, which have been proved to achieve a stable passivation effect on PS [45], the N₂ ambient achieved a repeatable stress evolution as shown in Figure 4.8. At these high flow rates, the effect of flow rate on film stress saturates and is no longer as significant as other factors such as temperature.

![Figure 4.13](Image)

**Figure 4.13** Comparison of PS film stress variation with N₂ flow rate from 20 sccm to 1000 sccm, at constant pressure of 1 atmosphere, under temperature of 375 °C and 475 °C.
A comparison of stress evolution of PS films annealed under different N₂ flow rate is shown in Figure 4.14. Low flow rate down to 20 sccm and high flow rate up to 1000 sccm were employed to demonstrate the difference derived from this factor. An initial hypothesis was that N₂ flow would perhaps cool the sample, so that higher temperatures would be required for low flow rate. However, the opposite was observed, which leads to the hypothesis of a velocity induced pressure differential. As shown in the plot, PS annealed at low flow rate achieves a similar stress evolution as that at high flow rate. However, for the 20 sccm result, a tensile stress peak occurs at a temperature of ~50 °C higher than that of the 1000 sccm flow rate as shown. Furthermore, no significant compressive stress peak was observed for the 20 sccm result, suggesting that high N₂ flow rate has a dramatic effect in enhancement of the hydrogen desorption. This is consistent with the observation of PS films annealed in vacuum, as discussed in Section 4.2.1.

**Figure 4.14** Comparison of PS stress annealed in N₂ at different flow rate and annealed in vacuum. All samples were measured in air.
Chapter 4

4.4 REPEATED ANNEALING EFFECT ON POROUS SILICON STRESS

Repeat passivation with the annealing technique discussed in Section 2.3.1 has been proved to be applicable to PS films [39], where the re-annealed PS film showed continued chemical stability. Furthermore, repeated annealing often occurs in scalable, integrated circuit fabrication processes. Therefore, it is necessary to understand how the stress evolves when the films experience repeated annealing, and how the structural stress of PS-MEMS could be tuned through repeated annealing.

A series of annealing and repeated annealing steps on PS stress are shown in Figure 4.15(a)-(b). In Figure 4.15(a), as-fabricated PS samples were initially annealed in N₂, 1000 sccm for 6 minutes at different temperatures \( T \), to passivate the film, which caused a stress variation along with annealing temperature as discussed in Section 4.2.1. Then a 15 s HF dip was utilised to remove the passivation (nitridation) layer of PS films, which for samples annealed at 550 \( ^\circ \)C or lower resulted in a return of the stress to a compressive state in the vicinity of the as-fabricated PS stress values as discussed in Section 4.2.2. Only samples annealed higher than 550 \( ^\circ \)C remained in tensile stress after the HF dip. For 475 \( ^\circ \)C annealed samples, the HF dip and re-annealing at different temperature treatments result in a repeated stress evolution similar to the first annealing, but with a decrease of compressive and tensile stress peak intensity.

On the other hand, in Figure 4.15(b), for 600 \( ^\circ \)C annealed samples, the HF immersion and re-annealing at \( T \) did not show a significant impact on film stress, which maintained at a value of stress in the vicinity of that observed after the first 600 \( ^\circ \)C annealing. In detail, slight reduction of residual stress was observed after HF immersion, changing from 2.0 MPa to 1.3 MPa after 15 s immersion and 1.1 MPa after 60 s immersion for the 600 \( ^\circ \)C annealed sample. Further decrease of stress was achieved through repeated annealing at 600 \( ^\circ \)C for the HF immersed PS films, but the stress was maintained as tensile. Even for 60 s HF immersion which would completely remove the nitridation layer on the PS [45], the stress of the re-passivated PS was in the vicinity of the first 600 \( ^\circ \)C annealed sample. These re-passivation results indicate that the PS film experienced a permanent structural change after 600 \( ^\circ \)C annealing, resulting in a stress...
that was subsequently fixed in the sample but independent of the nitridation layer itself. However, removal of the nitridation layer does render the film vulnerable to oxidation, so that long time (over 6 months) exposure to air of this PS film (600 °C annealed PS film after 60 s HF immersion) results in a compressive stress of approximately -2.6 MPa.

Figure 4.15  Annealing and repeated annealing effects on PS film stress. The annealing and repeated annealing were carried out in N₂, 1000 sccm for 6 minutes, at different temperatures (T). (a) Annealing, 15 s HF immersion after annealing, annealing at 475 °C+15 s HF immersion + repeated annealing at T; (b) comparison of annealing (passivation) at 600 °C, HF immersion and repeated annealing.
The effect on PS film stress of re-passivation under N\textsubscript{2} ambient has not been investigated before. Thus the outcomes of this study present an in-depth understanding of the re-annealing process, and provide a reference for stress control of PS-MEMS structure based on repeated passivation.

4.5 SUMMARY

Stress is a critical property for both fabrication and application of PS-MEMS structures. It can affect the optical, thermal, electrical and/or mechanical properties of the structures. Therefore, measurements of residual stress and methods of stress control are of significant interest in PS micromachining area, the investigation results provide references and instructions on stress evolution and control, rendering PS available in various applications through tuning of residual stress. Both X-ray diffraction rocking curve and radius of curvature-based methods were employed to study the residual stress of PS films.

Utilising X-ray diffraction rocking curve measurements, the lattice mismatch between the PS film layer and silicon substrate was acquired, which was utilised to calculate the stress. Control of stress through porosity change, ambient condition oxidation of PS, low temperature (<320 °C) annealing and HF immersion was studied with this method. The results show:

1) Porosity variation achieved by changing anodisation current density during fabrication can be a simple way of tuning the film stress;

2) Oxidation in air of as-fabricated and low temperature annealed PS can produce a tendency to compressive stress, which increases with time exposed to air;

3) The effect of low temperature annealing can be reversed by a short HF dip, which provides ways of adjusting the stress in PS films.

However, when the annealing temperature is higher than 320 °C, non-uniform lattice expansion/porosity results in the loss of the PS peak in XRD measurements, which renders this method no longer applicable for stress studies, and therefore another
method is needed. A key contribution of this work was in developing and validating (against XRD) a stress measurement method that worked for samples annealed up to 600 °C. Such temperatures are essential for stable passivation systems beyond nitridation, such as carbonisation [38].

Utilising radius of curvature measurements, investigations of PS film stress under high temperature annealing and other complex processes are possible. This method was undertaken to study the interrelated effect of hydrogen desorption, oxidation and nitridation, modified via annealing temperature and ambient, to understand the evolution of physical properties and the mechanism of the stress evolution. The results indicate that whether annealing in vacuum or nitrogen, the competition between tensile stress from hydrogen desorption and compressive stress from oxidation results in inflection points in the $\sigma$-$T$ data, with samples exhibiting either compressive or tensile stress depending on annealing temperature.

At high temperatures (above 500 °C) nitridation also prevents oxidation effects on stress. The effect of annealing on stress is largely reversed by a short HF dip, except in the case of nitridised samples annealed above 550 °C. Annealing at such temperatures with duration above 6 minutes is able to achieve relatively stable tensile stress in PS films, which is due to the significant nitridation layer formed on top of PS through annealing. For N$_2$ annealed PS films, the residual stress increases with N$_2$ flow rate from 20 sccm to 250 sccm, however this trend becomes less significant when flow rate is above 250 sccm. Both annealing duration and N$_2$ flow rate studies provide other options in stress control. The repeated annealing results of PS samples indicate that the PS film experienced a permanent structural change after 600 °C annealing, resulting in a fixed tensile stress in the sample.

The results in this chapter for the first time present residual stress in meso-PS films annealed under N$_2$ and vacuum at high temperatures up to 600 °C, which form the foundations for fabrication and evaluation of multistep PS-MEMS structures. The 600 °C annealed PS shows tensile stress of approximately 2.0 MPa, and remains tensile at 1.1 MPa after 60 s HF immersion. Furthermore, the 600 °C annealed PS presents stable tensile stress after at least 60 days exposure in air. The stress evolution of PS
under different treatments investigated in this chapter provides critical techniques in stress control of PS-MEMS structures.
CHAPTER 5
MICROMACHINED POROUS SILICON
STRUCTURE DESIGN AND FABRICATION

In this chapter, design and fabrication of PS-MEMS structures is presented. Released PS-MEMS structures with laterally uniform porosity and well defined profiles were successfully fabricated. In addition to utilising the processes developed in the earlier studies (presented in chapter 2), further investigation into and optimisation of the microstructure release processes was undertaken. Stress gradient was assessed as a design constraint and effectively limited through anodisation current control to compensate the vertical porosity gradient.

Though PS has shown significant potential for high sensitivity sensing and controllable transmittance/reflectance, very few applications utilising PS as the structural mechanical material have been developed. This is mainly due to the difficulty in achieving scalable, complex micromachining of PS with uniform porosity. To improve the sensitivity, optical efficiency and applicability of PS-MEMS, multistep PS micromachining processes are studied in detail in this chapter.

The multistep PS-MEMS fabrication processes are aiming to be compatible with conventional CMOS techniques and standard photolithography. In addition, diverse released PS microstructures and PS gratings were successfully fabricated based on the processes developed in this paper. The results in this chapter provide novel techniques in fabricating scalable, complex and uniform porosity PS microstructures.

5.1 RELEASED PS-MEMS STRUCTURE DESIGN

PS-MEMS structures have significant potential in sensing and optical applications due to the large surface area, tuneable refractive index and low residual stress in PS (on the
order of 1 MPa). However, with the low Young’s modulus of PS (on the order of 1 GPa) and the requirement for a pore filling process during photolithography, PS structures must be robust enough to survive the end-to-end processing. Other properties such as resonant frequency, refractive index and the air gap should be considered and controlled to fulfil the requirements of specific practical applications.

5.1.1 PS-MEMS structures

Various PS-MEMS structures have been designed for measurement and analysis in this work, including doubly clamped microbeams, cantilevers, Guckel rings (ring-and-crossbeam) [114], suspended trampolines and doubly anchored microbeams. A list of designed structures and their investigative purpose(s) is shown in Table 5-1.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Size</th>
<th>Purpose</th>
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</table>
| Doubly clamped microbeam                        | $100 \leq L \leq 500 \, \mu\text{m}$ | - Resonant frequency test  
                            | $20 \leq w \leq 40 \, \mu\text{m}$            | - Residual stress test |
| Cantilever                                      | $70 \leq L \leq 45 \, \mu\text{m}$  | - Resonant frequency test                    |
|                                                 | $20 \leq w \leq 40 \, \mu\text{m}$            | - Residual stress test                        |
| Guckel ring (ring-and-crossbeam)                | $100 \leq D \leq 1000 \, \mu\text{m}$ | - Residual stress test                        |
|                                                 | $20 \leq w \leq 30 \, \mu\text{m}$            | - Stress gradient test                        |
| Trampoline                                      | $100 \leq D \leq 300 \, \mu\text{m}$  | - Optical filter test                         |
|                                                 | $200 \leq L \leq 600 \, \mu\text{m}$            |                                             |
| Doubly anchored microbeams                     | $300 \leq L \leq 500 \, \mu\text{m}$ | - Eliminate impact of anchors  
                            | $20 \leq w \leq 40 \, \mu\text{m}$            | - Resonant frequency test |

*Table 5-1: Designed PS-MEMS structures*

The PS-MEMS structures were designed with lateral dimensions for various purposes, but with the same thickness of $t=2.5\pm0.1 \, \mu\text{m}$. However, the thickness can be adjusted through anodisation duration in the formation process, to make the structures suitable for applications with different thickness requirements.

The particular size range of each design was chosen to allow detection of PS microstructure properties with the available tools. For instance, the frequency of
released PS microbeams can be measured using laser Doppler vibrometry (0-1.5 MHz, which will be discussed in Section 6.3), but requires microbeam dimensions within the detectable range; transmission power of released trampolines can be detected through infrared optical reflectometry, but requires apertures of suitable size.

As a widely utilised and representative surface micromachining structure, the predominant focus of this chapter is PS doubly clamped microbeams. However, the design principle and fabrication processes are also suitable for other PS microstructures.

5.1.2 Stress effect on resonant frequency of doubly clamped microbeams

Resonant frequency is widely utilised in sensing applications [141, 142], as it is a very deterministic mechanical property of any surface micromachined structure. While it is known that residual stress can alter the fundamental stress-free resonant frequency, the impact of this stress on the resonant frequency of PS microbeams is unclear. The latter will be considered both theoretically and experimentally in this section.

For a doubly clamped microbeam, the fundamental flexural resonant frequency $f_0$ without considering internal stress is given by:

$$f_0 = 1.028 \frac{t}{L^2} \sqrt{\frac{E}{\rho}}$$  \hspace{1cm} \text{Equation 5-1}

where $E$ is the Young’s modulus, $\rho$ is the density, $t$ is the thickness and $L$ the length of microbeam. Here for the first time this form is applied to mesoporous PS microbeams by setting the modulus $E$ to be the Young’s modulus of the PS ($E=E_{ps}$) and the density $\rho$ is made the density of PS film. The Young’s modulus of PS is known to depend on porosity $P$ and is given by $E_{ps}=E_{si}(1-P)^3$, where $E_{si}$ is the Young’s modulus of the bulk Si (163 GPa) [4]; and $\rho$ is given by $\rho= \rho_{si}(1-P)$, where $\rho_{si}$ is the density of the Si substrate ($2.33 \times 10^3$ kg/m$^3$).

Figure 5.1 shows the impact on resonant frequency of controlling the porosity of a doubly clamped PS microbeam, compared with resonant frequency of a bulk Si microcantilever. For the same dimensions (200 $\mu$m×20 $\mu$m×2.5 $\mu$m) the PS microbeams show a dramatic decrease in the resonant frequency as porosity is increased.
This allows a single mask, whose dimensions have been defined, to create wafers containing thousands/millions of PS microbeams, where the resonant frequency of each wafer could be tuned simply by alternating the porosity of the film. This provides a great degree of process control in the formation of large-scale, matched sensor arrays. For an equivalent Si microbeam, post-design resonant frequency tuning could only be achieved by varying the thickness of the microbeam.

![Image of resonant frequency vs. porosity graph]

**Figure 5.1 Impact of PS porosity on resonant frequency of doubly clamped microbeam, microbeam size of 200 μm × 20 μm × 2.5 μm.**

Where cantilevers or doubly clamped microbeams are employed as a gas or biosensor (through detecting mass changes), it has been shown that the higher the resonant frequency of the beam, the higher the sensitivity to small changes in mass [36]. At first glance it may appear that PS microbeams do not offer a benefit here, as their resonant frequency actually decreased with porosity as shown in Figure 5.1. However returning to the analysis of Section 1.2, the change in the resonant frequency of a beam due to a change in mass of that beam is given by:

\[
\frac{df_0}{dm} = -\frac{f_0}{2m} = -1.028 \frac{t}{L^2} \left( \frac{1}{2m} \right) \frac{E}{\rho} = -1.028 \frac{t}{L^2} \left( \frac{1}{2Lw\rho_{si}(1-P)} \right) \frac{E_{si}(1-P)^3}{\rho_{si}(1-P)} \]

\[
= -1.028 \frac{1}{2L^3w_{si}\rho_{si}} \frac{E_{si}}{\rho_{si}} = S_m \quad Equation 5-2
\]
where $S_m$ is the sensitivity of the measurement to a mass change, and is shown to be independent of porosity. Hence, by using PS, the resonant frequency of the detection system can be lowered without compromising the sensitivity, by increasing the porosity. In some cases, it is easy and less expensive to detect frequency changes at low frequencies (kHz) compared to higher frequencies (GHz). This advantage combined with the very large surface area of the PS microbeam sensor (discussed in Section 1.2) renders this technology worthy of detailed study.

Beyond the modulus, density and dimensions of a material, when the internal stress of a released microbeam is considered, the fundamental frequency $f$ is modified as [143]:

$$f = f_0 \left(1 + \frac{0.295 \sigma L^2}{E t^2}\right) \quad Equation \ 5-3$$

where $\sigma$ is the internal stress of the beam. This relationship between resonant frequency of a microbeam and its internal stress can be transformed to yield an equation linear in terms of $L^{-2}$ given as [55, 143]:

$$f^2 L^2 = 1.057 \frac{t^2 E}{\rho l^2} + \frac{0.31 \sigma}{\rho} = a L^{-2} + b \quad Equation \ 5-4$$

where the slope of this linear relationship is given by $a=1.057t^2E/\rho$ and the y-axis intercept is given by $b=0.31\sigma/\rho$. Based on this transformed equation, it can be seen that given the density and dimensions of a microbeam, the Young’s modulus can be extracted from the slope and the residual stress from the offset when plotted as a function of $L^{-2}$. By measuring the resonant frequency $f$ of different beam lengths $L$, the linear relationship between $f^2 L^2$ and $L^{-2}$ has previously been utilised to extract material parameters for bulk Si as shown in Figure 5.2 [55].
Based on this relationship, both $a$ and $b$ can be determined through a simple linear least square method. Subsequently Young’s modulus and internal stress ($\sigma$) of PS can be extracted by using:

$$E_{ps} = \frac{a \rho}{1.057 t^2} \quad \text{Equation 5-5}$$

$$\sigma = \frac{b \rho}{0.31} \quad \text{Equation 5-6}$$

The stress and Young’s modulus extracted from these measurements can aid in understanding the impact of stress on the resonance using Equation 5-2 [143]. Based on theoretical modelling, a comparison of $f/f_0$ for doubly clamped microbeams fabricated with PS and with Si is shown in Figure 5.3. The $f/f_0$ data for the Si microbeams was extracted from previously published data [55]. The resonant frequency ($f$) includes the effect of residual stress while $f_0$ represents the resonant frequency without considering residual stress. All modelled microbeams (PS and Si) in the comparison utilised the same width of 20 $\mu$m and thickness of 2 $\mu$m; the PS film has a porosity of $P=81\%$. A tensile stress of 1.1 MPa was considered in the $\sigma$-$f$ model for the PS film, which would result from a 60 s immersion of N$_2$ annealed PS at 600 °C as determined in Section 4.4.
As shown in Figure 5.3, the resonant frequency of PS microbeams changed significantly when internal stress was considered. For a PS microbeam with a length of 480 μm, the frequency changed from 17.7 kHz to 60.5 kHz, resulting in a change by a factor of 3.4. Even for short PS microbeams of 100 μm, a 21% change is estimated (from 408.4 kHz to 493.8 kHz). Such dramatic changes in resonant frequency for such small changes in stress is characteristic of the high sensitivity of the PS microbeams, which is a significant motivation of this work. On the other hand, if the same residual stress is considered for a 480 μm long Si microbeam [55], only a 7% change of frequency is expected.

Therefore the effect of stress on the resonant frequency cannot be neglected when designing microbeams made from PS. However the models do support the supposition that these films would be highly sensitive to stress change due to adsorption of gas or vapour, providing a path to construct a highly sensitive stress sensor.

![Figure 5.3](image_url)  
*Figure 5.3* Comparison of $f/f_0$ of doubly clamped microbeams fabricated with PS and Si. $f$: resonant frequency considering residual stress; $f_0$: resonant frequency without considering residual stress. The $f/f_0$ data for Si microbeam was adapted from [55].
5.2 RELEASED PS-MEMS STRUCTURE FABRICATION

5.2.1 Released PS microstructure fabrication processes

Given the designs of the PS microstructures presented, fabrication processes can be carried out utilising techniques based on standard photolithography, as presented in Chapter 2. Generally the PS microbeam fabrication processes include PS film formation, N₂ passivation, photolithography to define anchor and beam structures, ICP-RIE, and repeated photolithography to define electropolishing regions, electropolishing and drying. The novel aspect of this work is that to release the PS films, a combination of repeated patterning, electropolishing and critical point drying is employed. This allows the creation of a truly all-silicon MEMS device. Specifics of the fabrication processes for PS microbeams will be discussed in this section in detail. The processes are also suitable for release of the other types of PS-MEMS structure that were detailed in Table 5-1.

For the PS film fabrication, room temperature anodisation was performed in a 15% HF/ethanol solution, typically with a constant current density of 10 mA/cm² for 403 s using p-type Si (resistivity of 0.9 Ω·cm). The current density and anodisation duration can be varied to achieve the desired porosity and thickness control, which will be discussed in Section 5.2.2. After formation, the PS film was subsequently annealed in a N₂ atmosphere at 600 °C for 6 min at 1000 sccm, to create low temperature annealed PS films with effective porosity \( P = 81 \pm 1\% \), and a physical thickness of \( t = 2.5 \pm 0.1 \) μm. The annealing process is critical as it makes the PS film suitable for direct photolithography processing using alkaline developer as discussed in Section 4.4. This type of PS was utilised in the work reported here, as its properties and annealing process has been previously comprehensively studied [39, 40].

Figure 5.4 shows the steps to form microbeam and anchor regions through the patterning process. To begin with, an anodised PS film was created and subsequently annealed under conditions described above, as shown in Figure 5.4 (a). After annealing, a layer of spin-on glass (SOG) was applied to the PS film prior to the application of the photoresist layer, to fill the pores, preventing photoresist seepage into PS (Figure 5.4...
For the PS film described above, the SOG (700B, 10.8% SiO₂ content, Filmtronics Inc., USA) was spun twice at a speed of 2000 rpm for 40 s each time. In Figure 5.4 (c), microbeams and anchors were defined using a standard positive photoresist photolithographic process using AZ EBR solvent (MicroChemicals GmbH, Germany) diluted positive photoresist AZ6632 (MicroChemicals, 20% solids content, ~0.85 μm thick). After photolithographic patterning, the SOG everywhere in the PS was removed by a short 10 s dip in 10% HF/ethanol, which resulted in an as-fabricated PS film selectively covered by photoresist, as shown in Figure 5.4 (d). Subsequently inductively coupled plasma reactive ion etching (ICP-RIE) was employed to rapidly etch (1 μm/min for the as-fabricated PS utilised in this work [73]) the PS film in the region not covered by photoresist to form the PS beam and anchor regions (Figure 5.4 (e)). ICP-RIE was carried out with a gas mixture of CF₄/CH₄ (31 sccm / 3 sccm) at a temperature of 25 °C. After etching, the positive photoresist was removed in acetone, leaving the patterned PS consisting of microbeams and anchors, as shown in Figure 5.4 (f). After that, a 5 s short dip in 10% HF/ethanol solution can be applied to remove any residual SOG in the structures.

N₂ annealed (600 °C for 6 min, at 1000 sccm) PS also allows multistep processing through repeated anodisation, annealing and photolithography to be performed [39]. Therefore, after the first patterning to form the PS anchor and microbeam regions, a second standard photolithographic process can be applied. Based on the types of masking layer for the release process (electropolishing), two different methods were investigated in this work for the repeated patterning.
Figure 5.4 First patterning step on PS to define anchor and microbeam regions. (a) After PS layer formation and passivation; (b) after SOG application; (c) after photolithographic process to define anchor and microbeam regions; (d) after removal of SOG; (e) after ICP-RIE to remove uncovered PS; (f) after photoresist removal to present PS anchor and microbeam regions.

A. Metal masking layer method.

Photoresist AZ2070 (MicroChemicals, 6.8 μm thick) was employed to define a metal mask pattern up to the anchor, as shown in Figure 5.5(a). A Cr/Au (10/200 nm) layer was subsequently deposited onto the anchor regions with a lift-off process based on a photoresist pattern, as shown in Figure 5.5(b). The photoresist was removed by a 15-minute N-Methyl-2-pyrrolidone (NMP) or dimethyl sulfoxide (DMSO) immersion and a 5-minute acetone immersion in the lift-off process. The metal region over the PS was important to define the anchors during electropolishing, as will be described later. Electropolishing with HF based electrolyte was carried out to etch the Si, and the electrolyte ensured any residual SOG in the pores was removed. Electropolishing was
carried out using a similar process to anodisation, but with different electrolyte (a 3% HF/DI solution) and electrical conditions (20 mA/cm², 180 s). After electropolishing, PS microbeams suspended on top of the Si substrate were formed (Figure 5.5 (c)) and the sample was kept submerged in electrolyte in the anodisation cell.

Figure 5.5 Repeated photolithography patterning and release of microbeams based on metal deposition and photoresist lift-off. (a) After photolithographic process to define metal anchor region; (b) after metal layer deposition and lift-off process to form metal anchor region; (c) after electropolishing to release PS microbeam.

B. Insulating photoresist masking layer method.

Instead of using metal deposition and photoresist lift-off to form a conductive masking layer in the repeated patterning, diluted positive photoresist AZ6632 (MicroChemicals, 20% solids content) utilised in the first patterning process was employed again for this method. An insulating masking layer pattern up to the anchor was defined through photolithography, as shown in Figure 5.6(a). To ensure the photoresist seeped into the pores of the PS and to increase the adhesion between the photoresist and the substrate, photoresist was spun twice onto the PS. After each spin the sample was rested for 10 min with a subsequent 5 min bake at 100 °C. A hard-bake for 2 h at 100 °C was employed after developing. This technique effectively eliminates the HF electrolyte infiltrating and attacking the interface between the Si and the photoresist, preventing photoresist delaminating from the substrate around the openings of the pattern. The long hard-bake after patterning was implemented to avoid bubbling and remove moisture in the photoresist, and to decrease side etching (undercut near anchors) and edge roughness of the electropolishing process [99], which will be discussed in detail in Section 6.2. With the photoresist mask patterned up to the anchor, the electropolishing
step was carried out. Due to the different electropolishing conditions for the insulating mask and the conductive mask, as discussed in Section 2.2, different electrolyte (a 5% HF/DI solution) and electrical conditions (15 mA/cm², 120 s) were applied in this process. After electropolishing, PS microbeams suspended on top of the Si substrate were formed (Figure 5.6(b)) and the sample was kept submerged in electrolyte in the anodisation cell.

![Figure 5.6 Repeated photolithography patterning with photoresist. (a) After photolithographic process to define photoresist anchor region; (b) after electropolishing to release microbeam.](image)

After electropolishing with either method A (metal masking layer) or B (insulating photoresist masking layer) as described, the sample in the anodisation cell was rinsed by DI water for 10 times, which guaranteed the removal of HF in the cell. For PS microbeams released with a photoresist masking layer, an extra immersion in acetone was implemented following the DI water rinses. The 5 min immersion in acetone removed the photoresist mask on PS and kept the PS microstructures clean. Subsequently, the sample was transferred to methanol which has a relatively low surface tension to reduce the capillary pull-down force [101], and kept in a methanol bath during the critical point drying process as discussed in Section 2.4.3 to release the PS doubly clamped microbeams.

### 5.2.2 Stress gradient control based on porosity change

Stress gradient is a common factor causing bending of released microbeams, which can significantly affect the performance of MEMS structures or even cause breakage. For PS micromachining in which the processes themselves can significantly affect stress of the film, as discussed in detail in Chapter 4, it is critical to understand the cause for the stress gradient and ensure a uniform stress in released PS microstructures.
Initially the cause of the stress gradient was investigated. In the PS formation process, there is a high anodisation rate of PS formed from the moderately doped wafers used in this work, causing a concentration gradient of HF solution near the interface between Si substrate and PS [40]. The high consumption of HF results in a low concentration of electrolyte at the reaction interface. It is known that HF concentration and current density are two key factors in determining the porosity of the PS layer during formation [45, 144]; lowering the HF concentration at a given current density will cause an increase in the porosity [145]. Therefore, an out-of-plane porosity gradient will be generated as shown in Figure 5.7, even with a constant applied current density and HF concentration.

![Figure 5.7 Porosity gradient formed in PS film layer.](image)

The detailed study presented in Section 4.1.1 showed that the stress in a PS film is related to its porosity. Therefore, with an out-of-plane porosity gradient in PS, the internal film stress is not uniform but instead presents as a stress gradient. Previous studies have reported PS anodised under DC conditions exhibited a 12(%)/µm porosity gradient [40]. This would cause up to 30% porosity change for the 2.5 µm thick PS film typically used in this work, and result in a top-to-bottom stress change of more than 10 MPa according to the $P-\sigma$ relationship detailed in this work and shown in Figure 4.2. Considering the very low Young’s modulus of the films on the order of 1 GPa ($P=81\%$), this stress gradient through the PS film will cause significant bending or breakage as shown in Figure 1.10.

A cantilever under a stress gradient ($d\sigma(z)/dz$) through the thickness ($z$ direction) of the microbeam will show vertical curved deflection as plotted in Figure 5.8(a). The reciprocal of the curvature, which equals the radius of a circle that passes through the points of the curve, as shown in Figure 5.8(b), is defined as the radius of curvature ($R$)
of the microbeam. The cantilever tip deflection ($\Delta d$) and the radius of curvature are critical factors to depict the bending of the cantilever, and can be expressed as [114]:

$$\Delta d = \frac{L^2}{2R} \quad \text{Equation 5-7}$$

$$\frac{d\sigma(z)}{dz} = \frac{2E\Delta d}{L^2} \quad \text{Equation 5-8}$$

where $L$ is the microbeam length and $E$ is the Young’s modulus.

The relationship between stress gradient and radius of curvature is plotted in Figure 5.9. As shown in the plot, the radius of curvature of the cantilever increases significantly with the stress gradient in film, which will result in dramatic bending of the structure. Therefore, a reduction of stress porosity gradient is required to control the stress gradient and fabricate flat microstructures.
Two effective methods in controlling porosity gradient have been previously reported [40], as shown in Table 5-2. The current compensation method has been employed to reduce the optical thickness gradient in PS distributed Bragg reflector (DBR) structures [146, 147] or investigate the depth homogeneity of PS porosity [148]; and the paused/pulsed anodisation method has been utilised as a technique to improve PS film porosity uniformity [149] or investigate the PS/Si interface roughness and photoluminescence effect of PS [150, 151]. However, no investigation on stress control with these methods has been reported.

Figure 5.9 Analytical model of the relationship between radius of curvature and stress gradient.
Table 5-2  Comparison of methods in [40] for controlling porosity gradient.

For a typical 2.5 µm thick PS film as used in this work, applying the ideal pulsed anodisation method with pulsing conditions of 5% duty cycle and 0.1Hz frequency [40] will dramatically increase the anodisation time, from 7 min with DC anodisation to over 140 min with pulsed current. Furthermore, the long immersion of PS in HF solution will cause an increase in porosity, which also needs to be accounted for. The long duration of the pulsed current method is its major drawback.

The alternative method which was ultimately used in this work is the current density compensation method, using real-time control of the applied current. This was chosen as a simple, convenient means of controlling the porosity during anodisation, with the aim of achieving the desired stress gradient compensation. To investigate the extent to which stress gradient was reduced through this method, Guckel ring (ring-and-crossbeam) structures as defined in Section 5.1.1 were fabricated with PS films formed under different current conditions. The Guckel rings were originally intended to enable tensile stress measurements on each sample, as previous measurements in Chapter 4 indicated the bulk stress of the films should be tensile. As shown in Figure 5.10(a), when a Guckel ring is under tensile stress, the central circular region will be stretched, causing a bowing of the central crossbeam which can be measured. However when a stress gradient is present, the structure will show a bending of the rings as shown in
Figure 5.10(b). Therefore the profile of the Guckel rings after being released indicates the stress profile in the microstructures.

![Figure 5.10](image)

*Figure 5.10  Guckel ring deformation under (a) residual tensile stress; (b) stress gradient. Images adapted from [152].*

In this work, continuously varied current density and anodisation time were implemented through a LabView program to tune the porosity. A comparison of the structures made with different PS films and a schematic plot of corresponding anodisation conditions is shown in Figure 5.11. In Figure 5.11(a), the PS film was formed under an applied DC current, and it can be seen from the SEM image that the low-yield PS Guckel rings were dramatically twisted due to significant stress gradient. In Figure 5.11(b), a two-step current density change was applied, stepping from 10 mA/cm² to 2 mA/cm², to change the porosity. This increased the Young’s modulus of the film and decreased the porosity gradient, resulting in suspended Guckel rings that were successfully released but still bending up significantly. In Figure 5.11(c), in which a multistep (continuously varying) current density, decreasing from 10 mA/cm² to 2 mA/cm², was applied during anodisation to compensate the porosity gradient, the Guckel rings showed much less bending deformation than those in Figure 5.11(b). The result of extending this multistep current density approach further by using a current density ranging from 20 mA/cm² to 2 mA/cm² is shown in Figure 5.11(d). This approach effectively eliminated the porosity gradient, resulting in flat Guckel rings as shown in the SEM image.
Figure 5.11 SEM images of microstructures and the corresponding current density applied to form the PS films. (a) DC current density at 10 mA/cm², (b) two-step current density of 10 mA/cm² and 2 mA/cm², (c) multistep current density ranging from 10 mA/cm² to 2 mA/cm², (d) multistep current density ranging from 20 mA/cm² to 2 mA/cm². Timescale varied for each applied current density and has been scaled to allow comparison.

In the growth of macro-porous silicon fabricated from n-type silicon, both theoretical and experimental studies have been used to confirm that out-of-plane porosity gradient on PS can be compensated by modifying etch current density with time [153], since the depth of pores (PS film thickness) is significantly affected by etching time and the HF
concentration at the pore tip. The work presented here confirms that the same principles apply to meso-porous silicon.

Since the change in HF concentration during anodisation alters the out-of-plane (vertical) porosity it is necessary to control the porosity in real-time during the application of the anodisation current density. To achieve this, the porosity $P(t)$ was modelled during anodisation as:

$$P(t) = (P_{max} - P_{min})e^{-ut/D} + P_{min} \quad \text{Equation 5-9}$$

where $v$ is the etch rate, $P_{min}$ is the minimum porosity and is determined at minimum current density $I_{min}$, $P_{max}$ is the maximum porosity and is determined at maximum current density $I_{max}$, $D$ is the spatial constant for the out-of-plane porosity change, and $t$ is the anodisation time. For instance, when the current density is set to range from 20 mA/cm$^2$ to 2 mA/cm$^2$, $P_{max}$=87% (at $I=20$ mA/cm$^2$) and $P_{min}$=71% (at $I=2$ mA/cm$^2$), and the etch rate varies from $v$=614 nm/min (at $I=20$ mA/cm$^2$) and $v$=82.5 nm/min (at $I=2$ mA/cm$^2$). The spatial constant $D$ was set to $D$=200 nm based on preliminary experiments which showed the largest radius of curvature at this value.

This work was supported by separate, detailed investigations on the relationship of etch rate $v$, porosity $P$ and current density $I$ as shown in Figure 5.12. During anodisation, the time ($t$) was recorded and the time index incremented according to $t=i\cdot\Delta\tau$, where $\Delta\tau$ is the time step, nominally set to 2 s during anodisation. At each time index $i$, the porosity was determined from Figure 5.12, and the current density obtained by comparison of the data in Figure 5.12 – this was the current that was applied during that time step. The etching depth $h$ was estimated from the running total of $h = \sum_i^n u_i \cdot \Delta\tau$, using the etch rate $u_i$ again estimated from porosity determined from Equation 5-9 at each time index $i$ according to Figure 5.12. The applied current was stopped when the estimated etch depth $h$ reached a value of 2.5 µm. The PS film formed with this method exhibited a measured thickness of 2.6 µm, indicating a good estimation of the etch rate corresponding to the different porosity and applied current at each time step.

These results indicated that the stress gradient was effectively eliminated through the control of the out-of-plane porosity distribution. It should be noted that the average
porosity (~73%) of the films also decreased using the applied current profile (from 20 mA/cm² to 2 mA/cm²) compared with the porosity (~87%) that results from an applied DC current (20 mA/cm²). However as shown in Figure 4.2, lower porosity films have even high overall stress, yet the Guckel rings remain flat even with the higher stress.

The surface profiles of two typical PS microstructures (Guckel ring and doubly clamped microbeam) are presented in Figure 5.13(a)-(b). The two structures were fabricated with the same PS film sample, and had the same beam length of 100 µm. It is known that if the Guckel ring is under tensile stress, the central crossbeam will bow due to stretching at both anchors, as shown in Figure 5.10(a), whereas it is unaffected by compressive stress. In contrast, when a doubly clamped microbeam is under tensile stress, it tends to be flat, but if it is under compressive stress, the microbeam will bow as discussed in Section 1.2.2. Figure 5.13(a) shows that the crossbeam in the PS Guckel ring has a root mean square (RMS) roughness of only 78 nm and is relatively flat, indicating the structure is under zero or compressive stress. In addition, Figure 5.13(b) shows that the PS doubly clamped microbeam is bowing up in the centre, indicating compressive stress exists in the microstructure. The compressive stress is believed to be due to the final stage HF electropolishing processes effectively removing the nitridation.

*Figure 5.12 Relationship between etch rate, current density and porosity of PS. The data was acquired from anodisation of p-type Si in 15% HF electrolyte.*
passivation layer from the PS surface, rendering the samples vulnerable to ambient oxidation [45]. As discussed in Section 4.4, long exposure of a HF immersed sample in air results in compressive stress of the PS film. Both microstructures were measured after being exposed to air for over 2 months, so that the oxidation would have shifted the residual stress into compressive stress and changed the microstructure surface profile.

The amount of compressive stress can be estimated using the relationship in Figure 5.14, where $R=2.76$ mm, $D=0.1$ mm and the film’s Young’s modulus is around 5 GPa. From this data the compressive stress is estimated to be 0.27 MPa. Comparing this to the stress evolution of N$_2$ annealed PS exposed to air shown in Figure 4.4, it can be seen that this compressive stress is negligible and within the uncertainty limits. Hence the stress balancing conditions presented are nearing the limit of optimisation.

Figure 5.13 Surface profile of released PS microstructures, measured by profilometer. (a) central crossbeam of Guckel ring; (b) doubly clamped microbeam.
Figure 5.14 Schematic plot for calculation of compressive stress in doubly clamped microbeams.

### 5.3 PS OPTICAL GRATINGS FABRICATION

PS has significant potential for optical applications because of its tuneable refractive index and low loss in the visible and infrared ranges. These advantages render PS a suitable candidate for optical chemical or biological sensing techniques such as using diffraction gratings. Previous studies on PS diffraction gratings typically employed two different methods:

1) Stamp technique, in which the PS layer is imprinted using a Si grating structure to form the PS gratings, creating sensitive diffraction sensors [154]. However, this technique causes densification of the porosity in the grating structure due to the stamping process, resulting in difficulties in modelling, characterisation and potentially particulate contamination.

2) Standard photolithography, in which PS diffraction gratings are fabricated based on N$_2$ (600 ℃, 6 min, 1000 sccm) annealed PS layer with ProLIFT pore filling and photolithography techniques [155]. Due to the limitations of the ProLIFT pore filling technique as discussed in Section 2.3.2, thick PS (>1 µm) grating structures with laterally uniform porosity have not be successfully fabricated with this technique. However, due to the low index of the film, relatively thick PS gratings are necessary for high diffraction efficiency in the infrared range.

The goal of this work is to demonstrate the feasibility of fabricating relatively thick (>1 µm) gratings in PS film with a small period (4 µm). To achieve this target, the pore
filling technique based on SOG, discussed in Section 2.3.2, was employed. A similar process to the first patterning discussed in Section 5.2.1 was carried out to fabricate the PS gratings, but with a grating mask of period \( \Lambda = 4 \mu m \) and duty cycle \( DC = 50\% \). The fabricated PS gratings are shown in Figure 5.15. Figure 5.15(a) shows that over 2 \( \mu m \) thick PS gratings were successfully fabricated through the standard photolithography with SOG pore filling technique. The improvements in the PS-MEMS fabrication process for this technique compared to previous studies [45], enables the possibility of fabrication of thick PS structures with aspect ratio of approximately 1:1. SEM measurements from Figure 5.15(b) shows that the gratings had a duty cycle of 0.6 due to the sloped side wall angle of 71\(^\circ\). The reason for the discrepancy between the designed (50\%) and measured (60\%) grating duty cycle is that the grating mask had a very small period of only 4 \( \mu m \), which required a high resolution photoresist patterned onto the PS. However, the available photolithography resolution and photoresists used could not achieve steep side wall grating patterns with this period. Further optimisation would be required to achieve the design targets, however the goal of achieving thicker grating structures has been successfully demonstrated by this work.

![Figure 5.15 SEM images of PS gratings fabricated through photolithography with SOG pore filling technique (beam voltage of 5 kV). (a) Fabricated PS gratings, (b) detailed measurements of PS gratings.](image)

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5.4 SUMMARY

Various PS microstructures were designed for different purposes. The structures included doubly clamped microbeams and Guckel rings were investigated in detail.

The effect of stress on resonant frequency of doubly clamped microbeams was analysed. Laterally uniform porosity PS microstructures were successfully released through a series of processes based on standard photolithography. This work significantly improves upon current macro-porous (typical pore size >50 nm) PS micromachining processes, showing the ability to fabricate scalable, complex PS-MEMS structures for surface micromachining.

Vertical stress gradient in PS microstructures was investigated and controlled with a unique technique of tailoring the current density during the PS formation process. For Guckel rings fabricated from PS formed this way, the stress gradient was effectively eliminated, resulting in a flat surface profile in the microbeams. This technique provides a novel, simple and quick method to tune the stress gradient in PS-MEMS micromachining process.

PS gratings were successfully fabricated, showing that the pore filling technique and PS-MEMS processes developed in this work are suitable candidates for fabricating PS microstructures with a thickness above 2 µm and aspect ratio up to 1:1. Such characteristics are extremely useful to achieve optimised grating performance in the infrared range which can leverage commonly available communication wavelengths around 1.5 µm.
CHAPTER 6
CHARACTERISATION OF RELEASED POROUS SILICON STRUCTURES

In this chapter, the focus is on the results obtained from released PS microbeams. Surface optical profilometry of released PS microbeams was used to characterise the release process and understand the properties of fabricated PS structures. Subsequently undercut of electropolishing under different masking layers was compared to investigate the optimum electropolishing masking layer. After implementation of the optimised release process in microstructure fabrication, high resonant frequencies of doubly clamped meso-PS microbeams were measured for the first time. Such measurements enable investigation of the effect of residual stress and an understanding of the resonant properties of released PS microstructures.

The evaluation in this chapter of the fabricated multistep PS-MEMS processes and microstructures reveals the significance of the technologies developed in this work. It shows new opportunities for fabricating complex PS microstructure that can be mechanically characterised and applied to sensing.

6.1 SURFACE PROFILE OF RELEASED PS MICROBEAMS

As discussed in Chapter 3, surface optical profilometry provides non-contact, topological characterisation of released PS microstructures. The profile of one of the released PS microbeams (fabricated using the processes described in Section 5.2.1) measured through optical profilometry is shown in Figure 6.1. The microbeams were 200 µm long and 20 µm wide. Electropolishing resulted in the doubly clamped microbeam being suspended approximately 2.6 µm above the Si substrate, giving a total
distance from the substrate to the PS top surface of 5.1 μm. For this beam the peak-to-valley (PV) variation in the surface topology was 340 nm, while the substrate PV variation after electropolishing was 130 nm, indicating the microbeam surface was relatively flat.

Figure 6.1 Surface profile of 200 μm long PS microbeams, measured through optical profilometry.

To complement the optical profilometry profiling, SEM was employed to acquire high resolution surface profiles of the PS microbeams fabricated in this work. Figure 6.2 shows an angled view SEM image of released PS microbeams, from which the full suspended profile including the air gap between the microbeams and Si substrate can be observed. The microbeams were 250 μm long and 20 μm wide. It can be seen from the SEM image that the Si under the microbeams exhibits smooth surface topography, indicating the electropolishing achieved uniform etching under the released PS
microstructures. Furthermore, with the high resolution available from SEM imaging, more details of the PS microstructures can be acquired, including the undercut which can be determined using a cross-sectional view. This will be discussed in Section 6.2.

![Angled view SEM image of released PS doubly clamped microbeams (Beam voltage of 5 kV).](image)

**Figure 6.2** Angled view SEM image of released PS doubly clamped microbeams (Beam voltage of 5 kV).

### 6.2 ELECTROPOLISHING UNDERCUT

Electropolishing has been used in this work as a key technique to release PS structures from the substrate. This technique avoids utilising the sacrificial layer that is commonly employed in other release micromachining processes, providing a unique method for releasing PS microstructures. However, as an isotropic chemical etching technique, electropolishing needs to be investigated and accurately controlled to prevent degradation or damage of released structures. To understand the electropolishing process for PS microstructure, various masks for electropolishing have been investigated by assessing their influence on etching behaviour and undercut.

For masks on p-type Si substrate similar to that used in this work, previous studies have investigated the different etching behaviour when using insulating masks compared to metal masks [63], as illustrated in Figure 6.3. For an insulating mask layer, a MIS (metal-insulator-semiconductor)-like sandwich structure is formed [63]. Due to the inhomogeneity that originates from the current concentration at the border of the masking layer, a depth profile at the edge that is deeper than in the middle of the etched structure results. For a metal masking layer, a diode-like structure is formed where a fraction of the current from the bulk can flow through the metal to the solution, resulting
in an isotropic etching profile. In this case, the undercut length is approximately equal to the etch depth.

\[ \text{Figure 6.3 Comparison of etching behaviour between different masking layers on p-type Si substrate. Image adapted from [63]. (a) Insulating masking layer, (b) metal masking layer.} \]

However, the findings illustrated in Figure 6.3 were related to PS film formation process (anodisation) on a Si substrate. The electropolishing of PS layers, although based on a similar technique to anodisation, shows different results. A comparison of electropolishing behaviour for various masks is shown in Figure 6.4. For Cr/Au (10/200 nm) metal mask layer on Si substrate (Figure 6.4(a)), the electropolishing shows an isotropic etching profile, where the ratio of the electropolishing undercut \( L_o \) versus etching depth \( d_o \) is approximately 1:1, which is consistent with previous reports [26, 63]. However, when the same metal masking layer was employed for PS film as discussed in Section 2.2.1, the metal layer did not prevent the HF solution from etching
Si under the edge of the mask, which caused a long undercut leading to detachment of the mask/PS layer from the Si substrate, as shown in Figure 6.4(b). For an insulating photoresist mask layer, the photoresist partially seeps into pores of PS and prevents the HF etching into those regions, decreasing undercut during electropolishing, as shown in Figure 6.4(c). To minimise the undercut, an adhesion improvement technique including photoresist thinning, double spins and long bakes as discussed in Section 2.4.2 was carried out, which effectively decreased the $L_o/d_0$ ratio from 7.5:1 (Figure 6.4(c)) to approximately 3.5:1, as shown in Figure 6.4(d).

![Figure 6.4 Comparison of electropolishing undercut for different masks on Si and PS. (a) Cr/Au mask layer on Si, (b) Cr/Au mask layer on PS, (c) photoresist mask layer on PS, (d) photoresist mask layer on PS, with adhesion improved.](image)

Therefore, electropolishing of PS thin films achieves significantly different results from the conventional electropolishing of bulk materials such as Si. The porous nature of the films from which the microstructures are to be made directly affects the electropolishing process and a method to minimise the undercut is required. In this work the photoresist adhesion technique as discussed in Section 2.4.2 effectively limited electropolishing undercut and improved the structure quality as shown by Figure 6.4(d). The quality and reproducibility of the undercut obtained using the photoresist adhesion technique
was found to be sufficient for the formation of released PS microstructures. However, the electropolishing undercut \( (L_o) \) versus etching depth \( (d_0) \) ratio (3.5:1) is still higher than ideal ratio (1:1) and methods for minimising the electropolishing undercut require further investigation but are beyond the scope of this work.

In addition, it has been reported that the anodisation process with frontside stress-free insulating masking layer (\( \text{Si}_x\text{N}_y \)) resulted in different current distributions and ion transport mechanisms when increasing anodisation time, which enabled the transformation of etching profile from edge-effect (convex) shape to concave shape as shown in Figure 6.5 [156, 157]. These studies also suggested that the etching time, mask thickness and opening dimensions could be factors to affect the etch shape. These studies provide additional methods for controlling the electropolishing profile apart from the change of masking layer type (conductivity) previously discussed with respect to Figure 6.3.

![Figure 6.5 Etch shape development in Si anodisation process with Si\(_x\)N\(_y\) mask: (a) schematic cross sectional view of Si during anodisation in HF; (b) etch shape after 1 min; (c) etch shape after 10 min. Images adapted from [156].](image-url)
6.3 RESONANCE MEASUREMENTS OF RELEASED PS MICROBEAMS

While stress is known to affect the resonant frequency of non-porous microbeams [54, 55], the relative impacts of stress when using low Young’s modulus PS films [42, 56] have not been experimentally characterised. This work aims to address this gap in understanding the effect of residual stress on resonance of PS microbeams. For the PS microbeams fabricated in this work, the measurement of resonant frequency was carried out through Doppler vibrometer system as discussed in Section 3.4.

The displacement-frequency spectrum of PS doubly clamped microbeams with different lengths \( L \) was measured as shown in Figure 6.6. The all-PS microstructures were fabricated through the processes detailed in Section 5.2.1, resulting in released PS microbeams with an air gap of approximately 2.5 μm. The PS was stress gradient compensated film (current density ranging from 20 mA/cm² to 2 mA/cm²) as discussed in Section 5.2.2. All microbeams were of the same 20-μm width and 2.5-μm thickness, with lengths ranging from 200 μm to 450 μm. The fundamental resonant frequency \( f_1 \) of each microbeam was identified from the highest peak in the spectrum for each corresponding measurement.

The measurements in Figure 6.6 show that the lowest (fundamental) resonant frequency \( f_1 \) decreased with increasing microbeam length as expected in Equation 5-1. The fundamental mode exhibits a high signal to noise ratio compared with the background noise. While a single resonant peak is expected, in some cases a secondary peak close to the first is observed. This secondary peak most likely arises due to the imperfect boundary condition caused by the undercut during electropolishing. As the length increases, a second peak well away from the fundamental mode frequency is observed at higher frequencies. The second longitudinal mode is expected at 2.5 times the fundamental frequency [158], however many of the higher order modes do not obey this relationship. These modes are most likely due to the torsional modes of the extremely flexible porous silicon microbeams.
Figure 6.6 Resonant frequency of PS microbeams with different length (L), measured through vibrometer in vacuum. (a) L = 200 \( \mu \text{m} \), (b) L = 250 \( \mu \text{m} \), (c) L = 300 \( \mu \text{m} \), (d) L = 400 \( \mu \text{m} \).
Subsequently the linear relationship between $L^{-2}$ and $f_1^2L^{-2}$ was plotted based on the data acquired from resonant frequency measurements, as shown in Figure 6.7. From the $f_1 - \sigma$ model as discussed in Section 5.1.2, the residual stress and Young’s modulus of PS film were extracted based on the model, yielding a residual stress of $|\sigma|=0.26\pm0.27$ MPa, and Young’s modulus $E_{ps}=4.2\pm0.9$ GPa, with a 95% confidence interval coverage. The statistical uncertainty of $\pm0.27$ MPa associated with the value extracted from Figure 6.7 provides important information regarding the stress variation across a range of microbeams. It is worth noting that the stress estimated from the bowing of a single microbeam shown in Figure 5.13(b) was -0.27 MPa (compressive), as discussed in Section 5.2.2.

This extracted stress obtained from fitting the linear relationship between $L^{-2}$ and $f_1^2L^{-2}$ does not indicate if the films are compressive or tensile. While highly compressive microbeams will not significantly vibrate, the small level of compressive (or tensile) stress being measured here can lead to misinterpretation of the data. The profile of the microbeam shown in Figure 5.13(b) suggests a slightly compressive stress in the films. While a stable low tensile stress (1.1 MPa) is expected from N$_2$ annealed PS film ($P=81\%$), HF immersion can degrade the passivation. As discussed in section 5.2.2, because the final process step was electropolishing via HF immersion, it is more than likely the passivation has been degraded leaving the PS vulnerable to oxidation. Subsequently this sample was exposed in air for approximately 3 days during the measurements, which could explain a slight compressive stress (decrease of tensile stress) present in the PS film.

The extracted Young’s modulus corresponds to a porosity of approximately 70% through $E_{ps}=E_{so}(1-P)^3$ \cite{4}. This porosity is lower than the typical 81% porosity used during much of this work and arose due to the use of the multistep current applied during anodisaton as shown in Figure 5.11(d).
A search of the available literature suggests that these are the highest resonance frequency released PS microbeams ever measured. Previous studies reported that PS microplates of 250×750 µm² to 2400×4000 µm² [42, 159] or 50×50 µm² to 150×150 µm² (with four supporting beams of 25×150 µm²) [53] have been successfully released, but only low frequencies (100 Hz-3 kHz) [42] were measured from those structures. In this work released PS microbeams as designed in Section 5.1 were fabricated and high resonant frequencies on the order of 100 kHz were measured, confirming the capability for small size, high frequency PS microstructure fabrication and measurement.

6.4 SENSING WITH PS MICROBEAMS

The successful release of uniform porosity PS microstructures provides opportunities for highly sensitive gas and vapour detection. As discussed in Section 1.2, the large surface area of PS provided by its porous structure enables PS microstructures to capture small amount of target gas or vapour, resulting in measurable changes in mass and other various mechanical properties. In this section, investigation into the sensing of vapours with released PS microbeams are presented, validating the potential for PS microstructures fabricated in this work to operate as sensors.
6.4.1 Sensing of vapour with PS microbeams

Figure 6.8 shows a schematic of the experimental setup in which sensing of isopropanol vapour using a microbeam constructed from meso-PS was carried out for the first time. The PS was formed with adjusted current density ranging from 20 mA/cm² to 2 mA/cm² as discussed in Section 5.2.2, resulting in a film with $P=73\%$ and $t=2.5 \, \mu m$ and little or no vertical stress gradient. Initially the PS microbeam was enclosed on the optical profilometer measurement stage along with a drop of isopropanol inside a chamber of fixed volume, as shown in Figure 6.8(a). After 15 min, all the solvent evaporated and was partially adsorbed by the PS microbeam, resulting in a vapour density of approximately $1.1 \times 10^{-3} \, mL/cm^3$ in the chamber. The cover of the chamber was subsequently opened for immediate measurement of the deflection. The deflection measurements were performed with an optical profilometer as discussed in Section 3.2.1. The profilometer allows the height change ($\Delta h$) of the microbeam to be measured over time, as illustrated in Figure 6.8(b).

![Figure 6.8 Schematic diagram of experimental configuration on optical profilometer stage for sensing of vapour with PS microbeam. (a) PS microbeam kept with a drop of liquid in a chamber, (b) chamber cover removed after completely evaporation of the liquid to allow beam deflection measured.](image)
Both released PS cantilever and doubly clamped microbeams were tested for sensing of isopropanol following the above approach. The height evolution during the tests of both microstructures are plotted in Figure 6.9(a)-(b). A cantilever with dimensions of 175 µm×30 µm×2.5 µm was employed, and the height was measured at its tip. The doubly clamped microbeam had dimensions of 300 µm×30 µm×2.5 µm, and the height was measured at the centre of the microbeam. As shown in the plots, both the cantilever and doubly clamped microbeam presented a significant height change after being exposed to isopropanol for 15 min, with a maximum deflection of 6.5 µm for the cantilever and 0.6 µm for the doubly clamped microbeam. This indicates the adsorption of the isopropanol caused a stress or stress gradient change within the microstructures. After the PS microstructures had been exposed to air for considerable time (up to 7 days), their heights decreased by only a very small amount and did not return to their original state. This suggests that the change caused by the isopropanol adsorption results in a permanent change to the material. From 4 hours to 48 hours exposure in air, the microbeam height change was less than 0.8 µm, and from 48 hours to 7 days exposure in air, ~0.2 µm height change was measured. This indicates that the change in the film properties caused by the vapour adsorption is much more significant than any change due to the ambient exposure, such as oxidation or temperature induced changes. In addition, it shows the height change after the isopropanol exposure is mainly due to the solvent, but not other factors. Apart from isopropanol sensing test, an acetone sensing test was carried out on the same cantilever subsequently, which showed similar results to the isopropanol test.

From this test, a drop of isopropanol (estimated to be 0.05 ml) in the chamber (of volume ~44.5 cm$^3$) resulted in the vapour density of 1100 ppm by volume (1.1×10$^{-3}$ ml/cm$^3$, ~1.5×10$^{-5}$ mol/cm$^3$), which caused a cantilever tip height change of 6.5 µm. If the relationship between the vapour density and the microbeam height change is linear, a vapour concentration of 169 ppm (2.3×10$^{-6}$ mol/cm$^3$) would account for a 1.0 µm change in the cantilever height, and could be measured through optical profilometry.
The study provides significant opportunities for improving the sensitivity in ultra-small concentration sensing, and proves that released PS microstructures fabricated in this work could be applied as a potential chemical sensor.

Figure 6.9 PS microbeam height evolution along with isopropanol adsorption and exposure in air. (a) Cantilever tip height change; cantilever length of 175 µm. (b) Doubly clamped microbeam centre height change; microbeam length of 300 µm.

6.4.2 Repeatability of sensing with PS microbeams

To understand the repeatability of sensing with the PS microbeam and the role of the adsorbed vapour in the structural change, further investigations were undertaken to repeat the sensing test on a PS cantilever with size of 175 µm ×30 µm ×2.5 µm.
The sensing test as demonstrated in Section 6.4.1 was carried out on the cantilever and repeated multiple times. After each period of vapour exposure, the height change achieved by the cantilever was recorded, and subsequently the sample was rested in air for 7 days to ensure the height of the microbeam had reached steady state. The height changes for each test are plotted in Figure 6.10(a)-(c). As shown from the data, the step height change of the PS cantilever decreased after each sensing test, suggesting that the vapour adsorption caused a structural change that saturated after repeated tests. In the 4th test and 5th test the cantilever even showed an initial decrease in height but no subsequent increase in height after being kept in the chamber with isopropanol – in the steady state the microbeam had apparently reached the limit of height change and therefore structural change due to the vapour adsorption.

Figure 6.10(b) also shows that in the 4th and 5th tests, exactly the same step height change of 1.4 µm initially occurred, followed by a return to the same steady state position as after the 3rd test, after evaporation of the vapour. In addition, for the cantilever height change in the first hour of each tests as shown in Figure 6.10(c), very good repeatability was observed in the 4th and 5th tests, indicating the microbeam reached a state of highly repeatable performance for vapour sensing.

The proposed explanation of the test results is that a balance of the gravity force and stress caused by the vapour adsorption (and then desorption/evaporation) was achieved in each of these latter tests, and that this process is repeatable. While stress changes in the material provides one mechanism for detection, a decrease in the PS-MEMS cantilever height may also be appropriate for measuring very small mass changes. The repeated sensing tests demonstrate the possibility to apply PS microbeams as sensors based on height changes when adsorbing target vapours. However the mechanism that leads to saturation of the PS cantilever height change has not been determined and is outside the project scope at this stage.
Figure 6.10  Repeated tests on PS cantilever for isopropanol sensing. (a) Normalised height variation with time for the duration of each test, (b) the maximum step height change after exposure to isopropanol in each test, (c) comparison of PS cantilever height change for the first hour in each test.
6.5 SUMMARY

As typical MEMS structures in surface micromachining, PS microbeams fabricated in this work were characterised with different techniques.

The surface profile of doubly clamped microbeams shows that those beams were successfully released and suspended on top of the Si substrate. The microbeams presented similar waviness to the substrate. In addition, more details from SEM images show that the electropolishing achieved uniform etching under the microbeams.

Comparison of electropolishing undercut with various masking layer shows that etch profiles after electropolishing through a layer of PS are different from that of etch profiles after electropolishing of bulk Si. Furthermore, the adhesion enhanced photoresist mask achieved the best undercut versus etching depth ratio, signifying this type of masking layer is the best option for electropolishing of PS structures.

The resonant frequency measurements of PS microbeams provided data to build the relationship between frequency and lengths of doubly clamped microbeams, from which the residual stress and Young’s modulus of PS were extracted. This is the first time such high frequency measurement of PS-MEMS structures has been demonstrated and it provides an opportunity for PS-MEMS sensing through frequency determination.

Released microbeams fabricated with uniform porosity PS film were investigated through static deflection measurements showing that solvent vapours were successfully detected with those microbeams. The study provides significant opportunities for improving the sensitivity in ultra-small concentration gas and vapour sensing, and proves that released PS microstructures fabricated in this work could be applied in a variety of chemical sensor applications. The repeated sensing tests on PS cantilevers showed that an initial mechanism causing height change, perhaps some sort of structural change, saturated, however it is unclear what the mechanism for the height change or its saturation was and whether it could be reversed.
CHAPTER 7
CONCLUSIONS AND FUTURE WORK

The primary goal of this work was to develop comprehensive multistep PS micromachining processes, and fabricate released PS-MEMS structures, utilising PS as the structural layer. The processes were investigated with CMOS compatibility in mind. In addition, investigation of PS and PS-MEMS structures was necessary for the assessment of the fabrication processes, including the residual stress and stress gradient. To achieve the goals, various techniques in scalable, complex surface micromachining processes were investigated and optimised. Evolution of residual stress in PS films under different treatments that would typically occur during the fabrication processes was investigated. Methods of tuning stress and stress gradient of PS film were developed. PS-MEMS structures were designed and fabricated. As a typical surface micromachining structure that is widely used in MEMS, doubly clamped PS microbeams were studied and characterised in detail.

All of the goals outlined in Chapter 1 have been achieved through research undertaken in this work, the key aspects of which are summarised and presented in this chapter, together with potential applications of the PS-MEMS structures.

7.1 OUTCOMES OF THE WORK

This work has developed comprehensive multistep processes for PS micromachining based on standard photolithography. The processes were designed with CMOS compatibility in mind and make PS available as a structural material in MEMS. This is the first time that all-PS microstructures with laterally uniform porosity have been successfully released and characterised. Furthermore, it is the first time the evolution of stress during PS-MEMS fabrication processes has been investigated in detail. Methods
of tuning PS stress and stress gradient have been developed in order to control the mechanical properties of PS structures.

Poorly defined features (significant under mask etching and non-uniform porosity), large structural size (1×1 mm²) and low aspect ratio (height : length <1:1) are all factors that will significantly limit the performance of PS-MEMS devices. Therefore, in Chapter 2, conventional MEMS techniques were analysed and their applicability to PS micromachining was investigated in the context of these factors. Optimised techniques to accomplish each step in a PS microstructure fabrication process were presented. Subsequently comprehensive PS-MEMS fabrication processes were developed. The major results from the investigation of PS micromachining processes are as follows:

- Pore filling utilising spin-on glass (SOG) renders thick (>1 µm) N₂ passivated PS compatible with standard photolithography.

- Conductive metal masks and insulting masks are both applicable for achieving patterning on PS structures, but they have limited applicability depending on the constraints of the particular structures and subsequent processing steps required.

- Electropolishing is a simple and convenient method for releasing PS structures, but the applied current needs to be adjusted for masks of different fill factors (ratio of the covered area to the whole area) or materials.

- Achieving a robust photoresist mask is critical for release of PS structures with high quality. A method was investigated and demonstrated to be suitable utilizing slow, controlled drying of the photoresist films.

By combining the above outcomes, comprehensive surface micromachining processes for releasing PS structures were developed.

Previous pore filling techniques resulted in a filler material that was difficult to remove or the technique was not suitable for thick (>1 µm) PS microstructures fabrication. Spin-on-Glass (SOG), which in the past has generally been applied as a coating or planarization layer in MEMS, was used for the first time as a pore filling material for meso-PS in this work. SOG allows well controlled exposure and developing time to be
achieved during photolithographic masking of PS by addressing the problem of photoresist removal from pores, and improves the controllability of patterning on PS via the exposure and developing processes.

Both conductive metal masks and insulating masks proved to be applicable for achieving repeated patterning on PS structures. The conductive metal mask in photolithography of PS can form good quality structures with steep sidewall, but they were found to only be suitable for applications that do not require the subsequent removal of the metal layer, and not recommended for electropolishing process due to significant under-mask etching. It was found for insulating masks there were various mask materials available for photolithography of PS, but the mask formation processes were generally complex, and simple photoresist masks were not suitable for long immersion in HF solution. However, in this work, because immersion times were not long (2-30 minutes), photoresist masks were the optimal option for release of PS microstructure with repeated patterning and electropolishing processes.

Electropolishing was shown to be a convenient technique for releasing PS structures due to its simple setup and easy controlled properties including etching depth (released gap). However, it should be noted that in optimising the electropolishing conditions for release of PS structures, any change in variables such as mask material or mask area must be taken into account.

In addition to optimising the electropolishing process, an effective method for enhancing photoresist mask durability in HF electrolyte and an effective drying process were both needed for release of PS structures, to avoid poor yield. For the former, a long bake after development enabled improved attachment of the photoresist to the substrate, which stopped HF etching of PS/Si under the mask. For the latter, critical point drying employing liquid CO₂ showed high process yield and no contamination of the sample.

To assess the fabrication processes developed in this work, an understanding of and method for evaluating the properties of PS films and microstructures is necessary. To enable this, suitable characterisation tools and techniques are required in the
investigation. Therefore, in Chapter 3, different techniques for characterisation of PS films and PS-MEMS structures were investigated. The major results from the characterisation techniques study are as follows:

- The X-ray diffraction (XRD) method is suitable for the study of residual stress in as-fabricated PS film and PS films annealed at temperatures no higher than 320 °C.

- The optical profilometry method used to measure radius of curvature (ROC) is suitable for the study of residual stress in high temperature (≥320 °C) annealed PS films, however the method requires removal of the PS layer to complete the radius of curvature analysis, so it is not suitable for repeat measurements on the same sample.

- Use of a surface profiler with a stylus will cause damage to the PS film. Optical profilometry and SEM are more suitable for acquiring surface profiles of PS films and PS microstructures compared to surface profiler.

- Reflectance spectrum measurements can provide porosity, thickness, refractive index and porosity gradient of the PS film. Chemical composition of PS films can be studied through the FTIR absorption spectrum technique.

As discussed, XRD was only suitable for measurement of samples annealed at temperatures up to 320 °C. For higher temperature annealing, no diffraction peak is obtained for the PS, most likely due to significant non-uniform lattice expansion/porosity induced by the annealing.

Radius of curvature measurements based on profilometry are suitable for high temperature (≥320 °C) annealed PS film stress analysis. But the analysis requires profilometry of the Si substrate (cleaved into rectangular shape) without PS layer, for which the PS films needs to be removed with KOH immersion. So this technique is unsuitable for subsequent measurements on the same PS sample.

Surface morphology characterisation was carried out through surface profiler, optical profilometry and SEM measurements. The profiler is suitable for height difference
measurement of different layers, but it will induce damage on PS film due to the stylus contact. Both profilometry and SEM can provide surface profile information without contacting the sample surface.

Controlling residual stress is critical in PS micromachining processes due to the low Young’s modulus of PS film and various treatments that would typically occur during the fabrication processes. PS microstructures exhibit a resonant frequency change, unwanted deformation or even breakage under significant stress or stress gradient. Therefore, both XRD and radius of curvature based methods were investigated to measure the PS film stress. Subsequently residual stress of PS films under different processing conditions was investigated, and methods of tuning the stress were presented. The major results from the investigation of PS film residual stress are as follows:

- Porosity variation achieved by changing anodisation current density during fabrication can be a simple way of tuning the film stress.

- Ambient oxidation of as-fabricated and low temperature annealed PS can introduce compressive stress to the film, and the compressive stress increases with time exposed to air.

- The competition between tensile stress from hydrogen desorption and compressive stress from oxidation resulted in inflection points in the stress-annealing temperature ($\sigma$-$T$) data.

- At annealing temperatures above 500 °C the nitridation prevents oxidation effects on stress. The effect of low temperature annealing was largely reversed by a short HF dip, except in the case of nitridised samples annealed above 550 °C.

- Annealing duration and flow rate were factors that can affect the PS film stress, providing options in stress control.

- Re-annealing results of HF-dipped PS samples indicated that the PS film experienced a permanent structural change after 600 °C annealing.
The relationship between porosity and residual stress built based on XRD measurements showed that porosity was an important factor in affecting the PS film stress. The results suggested that through changing the applied current during anodisation, the film residual stress can be adjusted accordingly.

XRD measurements after exposure of as-fabricated and 300 °C annealed PS to air indicated that oxidation of PS films could produce a tendency for compressive stress, as evidenced by an increase of existing compressive stress for as-fabricated PS, or a shift from tensile stress to compressive stress for low temperature annealed PS.

The N$_2$ annealing of PS film resulted in residual stress moving between compressive and tensile as annealing temperature was varied. By comparing with the H$_2$ desorption spectrum, it was concluded that the competition between tensile stress from H$_2$ desorption and compressive stress from oxidation results in inflection points in the $\sigma$-T data. Stress evolution with annealing temperature was determined by the combined effects of H$_2$ desorption, nitridation and oxidation.

At temperatures higher than 500 °C, N$_2$ annealed PS films showed tensile stress, suggesting that nitridation prevented oxidation and the compressive stress that arises from it. It was also found that the effect of annealing was largely reversed by a short HF dip, except in the case of nitridised samples annealed above 550 °C.

It was found that annealing duration and flow rate were factors that can affect residual stress in PS. However, when annealing duration was longer than 6 min or the flow rate was higher than 250 sccm, their effect on adjusting film stress was not significant.

The investigation showed that the PS film stress was relatively stable during the annealing, HF immersion, and repeated annealing processes at high temperature (600 °C). It was concluded that the PS film experienced a permanent structural change after 600 °C annealing, resulting in a stress fixed in the sample.

A series of PS-MEMS structures were designed in Chapter 5 for fabrication process evaluation and device investigations. Released PS microstructures were fabricated through multistep micromachining processes, subsequently the processes were
evaluated. The major results of the PS microstructure design and micromachining contributions are as following:

- The resonant frequency of doubly clamped microbeams was shown to be highly stress sensitive.

- Laterally uniform porosity PS microstructures were successfully released through a series of processes based on standard photolithography.

- Stress gradient due to vertical porosity gradient in PS film can be controlled through adjusting current during anodisation.

- PS gratings with thickness of about 2 µm and aspect ratio of ~1:1 were successfully fabricated

Through the modelling of stress versus frequency of doubly clamped microbeams, it was found that stress can change the resonant frequency by a factor of four (4) compared to the non-stressed frequency for 500 µm long PS microbeams. This indicated that the PS microbeams were highly stress sensitive, and supports the supposition that these structures are well suited for use as sensors based on adsorption induced stress change.

Laterally uniform porosity PS microstructures were successfully released through a series of processes based on standard photolithography. This work significantly improved the reported state-of-the-art processes, demonstrating the ability to fabricate scalable, complex PS-MEMS structures via surface micromachining.

Stress gradient in PS microstructures was investigated with a unique technique of tailoring current density during the PS formation process. The technique employs real-time control of current density and anodisation time to adjust out-of-plane porosity distribution, resulting in vertically uniform porosity. The uniform porosity effectively limited stress gradient in PS film. For fabricated Guckel rings, a flat top surface profile was obtained after complete characterisation of the applied current on the porosity and etch rate. This technique provides a new method in tuning the stress gradient in PS-MEMS micromachining processes.
PS gratings were also successfully fabricated, showing that the pore filling technique and PS-MEMS processes developed in this work are suitable candidates for fabricating PS microstructures with a thickness of 2 µm and an aspect ratio up to 1:1.

Chapter 6 presented investigations of the characterisation of PS microstructures fabricated in this work. In addition, the resonant frequency of released doubly clamped meso-PS microbeams was measured for the first time. The major results of characterisation of the PS microstructures are as following:

- PS microbeams were successfully released; the surfaces of those microbeams and the Si underneath were relatively flat
- Electropolishing with metal masks or photoresist masks can produce different results; the adhesion enhanced photoresist mask resulted in the least undercut during electropolishing
- High frequency of meso-PS microbeams was measured for the first time, from which the residual stress and Young’s modulus of PS were extracted

The surface profile of the doubly clamped microbeams showed that those beams were successfully released and suspended on top of the Si substrate. The microbeams presented similar curvature to the substrate. In addition, detailed profilometry and SEM studies showed that the electropolishing achieved uniform etching under the microbeams.

Comparison of electropolishing undercut with various masking layer materials showed that electropolishing on PS-covered-Si is different from that on bulk Si. Compared to electropolishing of bulk Si, PS-covered-Si resulted in longer undercut. Furthermore, adhesion enhanced photoresist masks achieved the best undercut versus etching depth ratio, making this type of masking layer optimal for electropolishing of PS structures.

The resonant frequency of meso-PS microbeams was measured for the first time, and the relationship between frequency and length of doubly clamped microbeams was determined. Subsequently the residual stress and Young’s modulus of PS were extracted.
Finally, the released uniform porosity PS microbeams were successfully applied to sensing of vapours, demonstrating that the released PS microstructures fabricated in this work could be applied to chemical sensing. Repeated sensing tests on PS cantilevers suggest that a saturation in the height change occurs after extended testing, however the mechanism for saturation and whether it could be reversed are still under investigation. Therefore, this work established comprehensive multistep PS micromachining processes, and successfully released PS-MEMS structures with uniform porosity, utilising PS as the structural layer. The residual stress and stress gradient of PS films were investigated, and methods in controlling both were developed. In addition, the PS microstructures were characterised, enabling further evaluation of the processes. Scalable, released mesoporous PS microstructures have been fabricated for the first time with uniform porosity and controllable stress. The PS microbeams fabricated based on the processes have also been shown to be applicable for vapour sensing.

7.2 FUTURE WORK

One of the aims of this work is to provide comprehensive PS-MEMS fabrication processes with CMOS compatibility in mind. Therefore, the reliability from wafer to wafer and uniform over the full wafer area should be investigated in the future. The detailed data could show the possibility of repeating the fabrication processes, and provide a reference for massive PS-MEMS production in microelectronics industry.

There are significant opportunities for investigations based on results of this work. With expansion of the experimental work and application of the results from this thesis, diverse MEMS devices utilising PS as the structural layer could be fabricated and characterised.

7.2.1 Fabrication of complex PS microstructures

A great number of PS-MEMS structures are possible for fabrication as a result of the PS micromachining processes developed in this work. For example, an extension of this work could be the fabrication of released multilayer PS microstructures.
The knowledge developed in this work to pattern PS films up to 2.5 µm thick enables the fabrication of patterned structures from multilayer PS, which could form an omnidirectional mirror with high reflectivity [160]. Through performing porosity control with alternating anodisation conditions (current density and/or HF concentration), multilayer PS could be formed on top of the Si substrate. In addition, uniform porosity and low stress of each layer can be achieved through tailoring the applied current conditions during anodisation. Subsequently multilayer PS could be released through PS micromachining processes developed in this work. The stress and stress gradient results of this work provide methods to balance the residual stress in multilayer PS, which would result in flat released PS microstructures with high yield. The structure could form a PS distributed Bragg reflector (DBR) mirror and MEMS-based tuneable Fabry-Perot filter with DBR [45], as shown in Figure 7.1.

The released porous multilayer films would allow analyte or gas filtration not only within the pores, but also within the gap between the bottom and top reflective DBR mirrors. The air gap between the DBR mirrors can be adjusted through control of electropolishing time as discussed in Section 2.4.1. The released layer (air gap) would allow easy ingress of vapours/gases and the DBR would allow vapours/gases to enter the pores. PS micro-cavities which are not released require slow diffusion of the vapour/gases through the top DBR layers into the central region of the micro-cavity, where the sensitivity of the micro-cavity is the highest. High finesse cavities require high reflectivity DBRs, needing many layers and as such, the response of these sensors is slowed. In the approach proposed here, using release DBRs with an air-gap, vapours/gases can rapidly enter the air gap, changing the refractive index in the gap and altering the centre frequency of the Fabry-Perot filter. Hence both high sensitivity (from high reflectivity multilayer DBRs) and rapid response (from the released DBR) would increase the sensing performance of micro-cavity devices. Furthermore, an all-Si optical filter can be fabricated through the processes, avoiding strain induced by other materials such as metal or polyimide typically used in forming high reflective released mirrors.
7.2.2 Investigation and utilisation of stress/stress gradient

The stress study of PS films under various treatments in Chapter 4 allows the understanding of factors affecting the PS residual stress, and the stress gradient control method investigated in Chapter 5 provides a path to fabricated flat PS microstructures with homogeneous internal stress. Therefore an expansion of the work could further enhance the ability to control and utilise the PS microstructures through stress and/or stress gradient.

Further expansion of the stress and stress gradient study could commence with developing a comprehensive model to understand the combined effects of various annealing conditions (annealing ambient, temperature, temperature ramp rate, susceptor lid height, gas flow rate, annealing duration, etc.) on PS film structure and the film stress. The physical (pore size and pore distribution) and chemical (composition, nitridation and carbonization) change of PS along with various treatments could be investigated through SEM, Energy Dispersive X-Ray Spectroscopy (EDS), XRD or other techniques, and incorporated in this model.
As discussed in Section 5.1.2, the PS microbeams are significantly stress sensitive compared to conventional Si microbeams. Further expansion of the stress effect investigation could also include the application of released PS-MEMS structures as tactile sensors as demonstrated in Figure 7.2 [161]. The tactile sensor has shown a promising future in applications with robotic fingers, and PS microsystems applied to this application could provide a rich data set by measuring the spatial distribution of contact forces [161]. With the ability to successfully release scalable meso-PS microstructures in this work, PS strain gauges are proposed to be fabricated and incorporated with existing robotic fingers. The utilisation of PS strain gauges could enable extremely small spatial stress differentials to be detected, therefore more delicate control and manipulation could be achieved than existing approaches.

Figure 7.2 Schematic diagram of tactile sensor. Image adapted from [161].

7.2.3 PS-MEMS sensing applications

With the ability to measure the resonant frequency of PS microbeams as discussed in Chapter 6, measurement of the frequency change of PS microbeams can be utilised for sensing applications. According to Section 1.1, the minimum detectable frequency change by the readout system is a major limitation for the minimum detectable mass density (MDMD), which determines the sensitivity of a mass sensing system, and is of significant importance for biological and chemical gas/vapour sensors. With the meso-PS (pore size 2-50 nm) investigated in this work, a surface area density of ~180 m²/cm³ could be achieved [76], which suggests that the surface area of a released PS microbeam
is $10^2$-$10^3$ times that of a Si microbeam of the same size. The large surface area enables the PS microbeam to adsorb significant amounts of biological/chemical targets, and the sensitivity is expected to increase by a factor of $10^2$-$10^3$ if the structure is functionalised uniformly.

Due to the large surface area of PS, a significant amount of the target analyte could be adsorbed onto the PS microbeam compared to the equivalent bulk microbeam, which would result in a significant shift in the resonant frequency. Therefore ultra-low concentration of targets could be detected through the easily measurable frequency changes expected from the PS microbeams. A proposed implementation of vapour sensing based on PS microbeams is illustrated in Figure 7.3. The PS microbeam could be electrically actuated to minimise external vibration noise (common mode noise). A resonant frequency shift could be detected by a vibrometer when a small amount of vapour is present.

![Figure 7.3 Schematic demonstration of vapour sensing based on PS microbeam resonant frequency measurement.](image)
A similar implementation could be utilised to achieve ultra-sensitive temperature sensing based on PS microbeam resonant frequency. As discussed in Chapter 4 and Chapter 5, residual stress in PS film depends on temperature, and hence the resonant frequency of PS microbeams, which is significantly stress sensitive, would subsequently change with the temperature. By integrating both gas/vapour sensing and temperature sensing, ultra-sensitive, temperature independent vapour sensing could be achieved. Dynamic mode sensing is not the only possibility. Static mode sensing as discussed in Chapter 1 could be used as the surface profile would change due the thermal expansion of PS [162]. Therefore, this platform provides a simple method for high sensitivity temperature and gas/vapour sensing.

7.3 SUMMARY

This thesis has developed comprehensive PS micromachining processes which enable the fabrication of scalable, complex PS-MEMS structures, in which uniform porosity PS serves as the structural layer. A series of improvements of current PS micromachining processes have been presented, including SOG assisted photolithography on PS, release of uniform porosity PS microstructures through electropolishing, and adhesion enhanced photoresist masking layer for electropolishing. Thick (~1-2.5 µm) PS microstructures with uniform porosity were fabricated. All-silicon based (PS) microstructures were successfully released, without requiring oxide or other release layers. The PS film residual stress evolution though various treatments was investigated and methods in tuning the film stress and stress gradient were developed. Preliminary sensing of vapours using PS structural layers was successfully carried out with released cantilever and doubly clamped microbeams. Combining the developed PS micromachining processes, and film stress and stress gradient control methods will enable fabrication and application of diverse new PS-MEMS sensing technologies.
References


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