Novel Strategies for Surface Micromachining TiN Thin Films Deposited by Filtered Arc

by

Andrew John Dowling

A thesis submitted for the degree of Doctor of Philosophy at the Industrial Research Institute Swinburne Faculty of Engineering and Industrial Sciences Swinburne University of Technology Australia

(March 2005)
Abstract

TiN is used commercially as a wear resistant coating on cutting tools and as a diffusion barrier in microelectronics. TiN has gained increased interest as a material for MEMS, however there has been very little work carried out in the area of patterning and releasing TiN for use as a structural MEMS material.

This thesis presents an investigation into the patterning and release of filtered arc deposited TiN thin films using surface micromachining techniques. Two novel strategies are presented for patterning TiN thin films and are achieved using excimer laser micromachining and photolithographic wet-etching.

TiN was deposited onto single crystal Si and Cr and Cu sacrificial layers on Si. The use of Cr as a sacrificial layer was found to facilitate the best quality patterning of the TiN and hence the majority of the work involved using Cr sacrificial layers.

TiN was deposited using partial filtration and full filtration and differences in the ability to selectively laser pattern the TiN from the Cr sacrificial layer are presented. Various analytical techniques were employed to investigate the origin of the difference in laser patterning the TiN thin films.

The establishment of TiN and Cr as a novel material combination for surface micromachined MEMS was extended by etching the Cr sacrificial layer to facilitate the release of TiN stress-measurement structures.

The major finding of this thesis is that filtered arc deposited TiN thin film on Cr can be used as a material combination to surface micromachine freestanding TiN structures as high quality patterning and etch selectivity can be achieved using both excimer laser micromachining and photolithographic wet-etching.
Acknowledgements

I would like to express my sincerest gratitude to my supervisors, Professor Erol Harvey and Professor Derry Doyle for their expert guidance, friendly encouragement and patience during the course of this work. It has been a privilege to be a student of both of these gentlemen and I am deeply grateful for their efforts over the years. Of importance has been their assistance in forming the literary part of this work.

I wish to give special appreciation to Associate Professor Muralidhar Ghantasala for his tireless contribution to my understanding of the field of materials for micromachining and input into this thesis and publications. His calm demeanour and unfailing enthusiasm often served as a directional beacon and I am truly grateful for his assistance and friendship.

A special thank you to Surface Technology Coatings for providing access to the filtered arc deposition unit. In parallel, I would also like to thank Mr. Andrew Vlasveld for both practical and theoretical assistance in the area of filtered arc deposition and vacuum technology.

I wish to express a special thank you to Dr. Jason Hayes of Swinburne University of Technology for his guidance and assistance in the area of excimer laser micromachining.

The following researchers from the Australian Nuclear Science and Technology Organisation (ANSTO) deserve many thanks; Dr. Peter Evans for his expert assistance in the area of RBS; Dr. Ken Short for his expert assistance in the area of XRD and Dr. Kathryn Prince for her expert assistance in the area of SIMS. Both Dr. Peter Evans and Dr. Ken Short went beyond their call of duty and for that I am grateful.

I would like to thank both Mr. Hans Brinkies of Swinburne University of Technology and RMIT University Applied Physics for SEM and EDS analysis.

Many thanks need to go to Professor Ronald Lawes, retired head of the Central Microstructure Facility (CMF) at the Rutherford Appleton Laboratories (RAL) for his hospitality during my study trip to the United Kingdom.
I would like to acknowledge Swinburne University of Technology for facilitating this field of study through the designation of the Vice Chancellor’s Research Scholarship from which I received financial support.

I would also like to acknowledge the assistance provided by ANSIE grant No. 01/170 that facilitated research activities at ANSTO.

Finally, I would like to thank my family and friends for their support, understanding and patience during this undertaking. Their generosity and companionship has been greatly appreciated.
Declaration of Originality

This theses contains no material which has been accepted for the award of any other degree or diploma in any university, and to the best of my knowledge contains no material previously published or written by another person, except where due reference is made in the text of the theses. Work based on joint research or publications in this thesis fully acknowledges the relative contributions of the respective authors or workers.

Signed ........................................

Andrew John Dowling

Date  .............................
Table of Contents

1 Introduction 1
  1.1 MEMS and Integrated Microsystems 1
  1.2 Micromachining 2
  1.3 Surface Micromachining 2
  1.4 Surface Micromachining and Integrated Microsystems 4
  1.5 Motivation for TiN 4

2 Literature Review 6
  2.1 Thin Film Deposition 6
    2.1.1 Chemical Vapor Deposition 6
    2.1.2 Plasma and Plasma Processing 7
      2.1.2.1 DC Diode Discharge 7
    2.1.3 Physical Vapor Deposition 8
      2.1.3.1 Sputtering 9
      2.1.3.2 Cathodic Arc Evaporation 10
      2.1.3.3 Filtered Arc Deposition 11
    2.1.4 Pulsed Laser Deposition 12
  2.2 Microlithographic Etching 13
    2.2.1 Wet-etching 14
    2.2.2 Dry Etching 15
  2.3 Laser Micromachining 16
    2.3.1 Nd:YAG 19
    2.3.2 Ti:sapphire 20
    2.3.3 Excimer Laser 21
    2.3.4 Pulsed Laser Ablation 22
    2.3.5 Thin Film Ablation Mechanisms 23
2.3.6 Selective Laser Micromachining of Thin Film Systems 23

2.4 Residual Stress in Thin Films 25

2.5 Measuring Stress in Thin Films 26

2.6 Uses of TiN Thin Films in MEMS 28

2.7 Physical Properties of TiN 30

3 Experimental Methodology 31

3.1 Substrate 31

3.2 Magnetron Sputtering 32

3.3 Filtered Arc Deposition 32

3.4 Excimer Laser Micromachining 35

3.5 UV Photolithography and Wet-etching 36

3.6 Scanning Electron Microscopy (SEM) 38

3.7 Laser Scanning Confocal Microscopy (LSCM) 39

3.8 Rutherford Backscattering Spectroscopy (RBS) 39

3.9 X-Ray Diffraction (XRD) 42

3.10 Secondary Ion Mass Spectrometry (SIMS) 43

4 Laser Patterning of Partially Filtered TiN Thin Films 46

4.1 Characterisation of Partially Filtered TiN 46

4.2 Selective Removal of TiN Thin Film 53

4.3 Laser Patterning of TiN from Underlying Materials 55

4.3.1 Si (100) Substrate 55

4.3.2 Cu Sacrificial Layer 56

4.3.3 Cr Sacrificial Layer 57

4.4 Laser Patterning of TiN on Cr Sacrificial Layer 59

4.4.1 Selective Removal of TiN Thin Film 59
8 Conclusions and Suggestions for Future Work  123

References  126

Index  A-1

Publications  A-3

ix
List of Figures

Chapter 2

2.1 Schematic of (a) DC diode discharge and (b) DC potential distribution across the DC diode discharge.
2.2 Potential new high-resolution lithography tools.
2.3 Schematic representation of the laser irradiation and ablation of a polymer.
2.4 TiN coated Si cantilevers, deflected by high compressive stress in the TiN film.

Chapter 3

3.1 Schematic of the filtered arc deposition system showing partially filtered configuration.
3.2 Schematic of the filtered arc deposition system showing fully filtered configuration of a 22º knee.
3.3 Block diagram showing the excimer laser system.
3.4 Laser micromachining steps used to pattern TiN from Cr and Cu layers showing (a) excimer laser irradiation, (b) the patterned TiN thin film on a sacrificial layer.
3.5 Fabrication steps used to wet-etch TiN showing (a) exposure of photoresist with mask aligner radiation, (b) etching of the Cr contact mask, (c) etching TiN thin film on sacrificial layer, (d) contact mask removal and sacrificial etch of Cr to release TiN structure.
3.6 Schematic of beam-specimen interaction of RBS analysis.
3.7 Schematic representation of the 600 µm × 600 µm feature in a 6 × 6 array used to provide an irradiated area of approximately 13 mm² for the purpose of RBS analysis.
3.8 Schematic of diffraction of X-rays from a set of crystal planes.
Chapter 4

4.1 RBS spectra (experimental and simulated) showing a 554 nm thick TiN\textsubscript{1.0} film on Si.

4.2 SEM micrograph of a cross-section of a ~9 \textmu m thick partially filtered TiN thin film on Si showing the columnar structure of the TiN through the presence of parallel rod-shaped grains.

4.3 XRD spectrum of Si (100) substrate showing the Si (200) and Si (400) peaks at \(2\theta = 38.5^\circ\) and 73.2\(^\circ\).

4.4 XRD spectrum of partially filtered TiN deposited at room temperature on Si showing three possible TiN peaks; (111) at \(2\theta = 42^\circ\), (200) at \(2\theta = 50^\circ\) and (220) at \(2\theta = 73.3^\circ\). The preferred orientation of the TiN is (111).

4.5 XRD spectrum of partially filtered TiN deposited at room temperature onto Cr on Si showing a TiN (111) preferred orientation.

4.6 XRD spectra of partially filtered TiN deposited at room temperature and 200\(^\circ\)C. Both spectra show that the TiN has a (111) preferred orientation.

4.7 SIMS spectra of partially filtered TiN deposited onto Cr at room temperature showing TiN/Cr interface to be around 147 nm thick.

4.8 SIMS spectra of partially filtered TiN deposited onto Cr at 200\(^\circ\)C showing TiN/Cr interface to be around 100 nm thick.

4.9 (a) Confocal micrograph of a ~554 nm thick partially filtered TiN thin film on Si laser patterned at a fluence of 1.60 J/cm\(^2\) using eight pulses (b) EDS spectrum obtained from the patterned region.

4.10 (a) Confocal micrograph of ~400 nm thick partially filtered TiN thin film on a ~700 nm thick Cu sacrificial layer on Si laser patterned using a 20 \textmu m feature at a fluence of 1.50 J/cm\(^2\) using one pulse (b) EDS spectrum indicating exposure of the Cu sacrificial layer.

4.11 (a) SEM micrograph of ~420 nm thick partially filtered TiN thin film on a ~1000 nm thick Cr sacrificial layer on Si laser patterned using a 20 \textmu m feature at a fluence of 1.60 J/cm\(^2\) using one pulse (b) EDS spectrum showing only Cr peaks indicating the selective removal of the TiN thin film.
4.12 Confocal micrographs of a ~554 nm thick TiN thin film on Si (100) substrate laser patterned with a 15 µm feature at a fluence of 1.60 J/cm² using (a) 32 and (b) 64 pulses.

4.13 Confocal micrographs of ~400 nm thick TiN thin film on a ~700 nm thick Cu sacrificial layer on Si laser patterned using a 20 µm feature at a fluence of 1.50 J/cm² using (a) one pulse (b) two pulses and (c) four pulses.

4.14 SEM micrographs of ~420 nm thick TiN thin film on a ~1000 nm thick Cr sacrificial layer on Si laser patterned using a 20 µm feature at a fluence of 1.60 J/cm² using (a) one (b) two and (c) four pulses.

4.15 SEM micrographs of a TiN cantilever laser patterned at a fluence of 1.22 J/cm² into a ~420 nm thick TiN thin film on Cr showing (a) the entire cantilever and (b) a section of the edge showing extremely high quality patterning.

4.16 SEM micrograph of a RBS sample of ~425 nm thick TiN thin film on a ~1000 nm thick Cr sacrificial layer showing laser patterning at a fluence of 1.22 J/cm² using one pulse.

4.17 RBS spectra (experimental and simulated) showing the presence of a Cr film with 17% O. Laser patterning was carried out at a fluence of 1.22 J/cm² using one pulse per area.

4.18 SEM micrograph of ~420 nm thick partially filtered TiN thin film on Cr on Si laser patterned using a 20 µm feature at a fluence of 1.60 J/cm² using one pulse showing a crack in the Cr film induced by the laser patterning process.

4.19 Micrographs of TiN on Cr on Si, laser patterned using a single pulse at fluences of (a) 1.60 J/cm² (SEM micrograph) (b) 1.22 J/cm² (SEM micrograph) and (c) 0.99 J/cm² (confocal micrograph).

4.20 RBS spectra (experimental and simulated) of partially filtered TiN on Cr on Si after laser patterning using one pulse per area at fluences of (a) 1.22 J/cm² and (b) 0.99 J/cm².

4.21 SEM micrographs of TiN on Cr laser patterned using a single pulse with test features of (a) 15 µm irradiated at 1.22 J/cm², (b) 10 µm irradiated at 1.22 J/cm², (c) 7.5 µm irradiated at 1.22 J/cm², (d) 5 µm irradiated at 1.22 J/cm², (e) 2.5 µm irradiated at 1.22 J/cm².

4.22 RBS sites of partially filtered TiN laser patterned at a fluence of 1.22 J/cm² using (a) one pulse (b) two pulses and (c) four pulses.
4.23 RBS spectra (experimental) of partially filtered TiN on Cr on Si laser patterned at a fluence of 1.22 J/cm² using one, two and four pulses per area. The spectra show the presence of a Cr film only on Si, indicating the selective removal of the TiN thin film.

4.24 SEM micrograph showing a TiN cantilever laser patterned at a fluence of 1.22 J/cm², on a Cr layer (~400 nm thick) on Si showing that no damage has been induced to the Cr layer.

4.25 SEM micrographs of a ~440 nm thick TiN thin film on Cr laser patterned with a 20 μm feature at a fluence of 1.53 J/cm² using (a) one and (b) two pulses. Both micrographs show that the TiN thin film was not selectively removed.

4.26 SEM micrograph of a ~440 nm thick TiN thin film on Cr laser patterned with a 20 μm feature at a fluence of 1.53 J/cm² using four pulses showing partial TiN thin film removal and severe damage induced on the Cr sacrificial layer.

4.27 SEM micrographs showing a ~380 nm thick partially filtered TiN thin film (and corresponding EDS spectra) laser patterned at a fluence of 7.4 J/cm² using (a) one pulse (b) two pulses and (c) four pulses.

4.28 RBS spectra (experimental and simulated) of a ~380 nm thick partially filtered TiN thin film on Cr on Si in (a) the deposited state and (b) after laser patterning at a fluence of 7.4 J/cm² with one pulse per area.

4.29 (a) SEM micrograph of a ~380 nm thick partially filtered TiN thin film on Cr on Si laser patterned at a fluence of 7.4 J/cm² showing cracking of the TiN thin film and regions of exposed Si substrate (b) an EDS spectrum showing Ti, Cr and Si peaks (c) an EDS spectrum showing a Si peak only.

Chapter 5

5.1 RBS spectra (experimental and simulated) showing a ~360 nm thick TiN₁₀ film deposited under fully filtered conditions on Cr on Si.

5.2 XRD spectrum of showing TiN with a (220) preferred orientation.

5.3 SIMS spectra of TiN deposited under fully filtered conditions onto a Cr film showing the TiN/Cr interface to be approximately 180 nm thick.
5.4 (a) SEM micrograph of a ~255 nm thick fully filtered TiN thin film on Cr laser patterned at a fluence of 2.03 J/cm² using a single pulse (b) EDS spectrum indicating an exposed Cr layer.

5.5 (a) SEM micrograph of a ~72 nm thick fully filtered TiN thin film on Cr laser patterned with one pulse at a fluence of 1.41 J/cm² and (b) EDS spectrum obtained inside the laser patterned region.

5.6 SEM micrographs of a ~255 nm thick fully filtered TiN thin film on Cr laser patterned using one pulse at fluences of (a) 2.16 J/cm² (b) 2.03 J/cm² (c) 1.22 J/cm² and (d) 1.04 J/cm² showing a reduction in patterning quality with decreasing fluence.

5.7 RBS spectra (experimental and simulated) of a ~72 nm thick fully filtered TiN thin film on Cr on Si in the as deposited state.

5.8 (a) SEM micrograph of a ~72 nm thick fully filtered TiN thin film laser patterned at a fluences of 0.725 J/cm² with one pulse (b) EDS spectrum indicating the presence of exposed Cr.

5.9 (a) RBS spectra (experimental and simulated) of a ~72 nm thick fully filtered TiN thin film on Cr on Si laser patterned with one pulse per area at a fluence of 0.58 J/cm² and (b) SEM micrograph of a region irradiated at 0.58 J/cm² using one pulse showing incomplete removal of the TiN thin film.

5.10 RBS spectra (experimental and simulated) of a ~72 nm thick fully filtered TiN thin film on Cr on Si laser patterned with one pulse per area at a fluence of 1.22 J/cm².

5.11 (a) SEM micrograph of a ~360 nm thick fully filtered TiN thin film laser patterned with one pulse at a fluence of 2.16 J/cm² (b) EDS spectrum of the laser patterned region showing the presence of TiN and dominant Cr peaks.

5.12 SEM micrographs of a ~360 nm thick fully filtered TiN on Cr laser patterned using one pulse at fluences of (a) 0.87 J/cm² (b) 1.22 J/cm² and (c) 2.16 J/cm² with corresponding EDS spectra showing a reduction in the size of the Ti Kα peak with increasing laser fluence.

5.13 RBS spectra (experimental and simulated) of a ~360 nm thick fully filtered TiN thin film on Cr as deposited and laser patterned using one pulse per area at fluences of 0.87, 1.22 and 2.16 J/cm².
5.14 SEM micrographs of a ~360 nm thick fully filtered TiN thin film laser patterned at a fluence of 2.16 J/cm$^2$ using (a) one pulse (b) two pulses (c) four pulses and (d) eight pulses. The micrographs show increasing thermal damage with number of pulses.

5.15 (a) SEM micrograph of a ~360 nm thick fully filtered TiN thin film laser patterned at a fluence of 2.16 J/cm$^2$ using two pulses (b) EDS spectrum of the patterned region indicating the detection of Cr only.

5.16 SEM micrograph of a ~360 nm thick fully filtered TiN thin film on Cr laser patterned at a fluence of 1.22 J/cm$^2$ using two pulses.

5.17 RBS spectra (experimental and simulated) of ~360 nm thick fully filtered TiN on Cr laser patterned at a fluence of 1.22 J/cm$^2$ using two pulses per area.

5.18 SIMS spectra of TiN/Cr on Si laser patterned at a fluence of 1.22 J/cm$^2$ using two pulses.

5.19 SEM micrographs of fully filtered TiN thin films laser patterned at a fluence of 2.16 J/cm$^2$ and having thickness of (a) ~75 nm (b) ~255 nm (c) ~360 nm and (d) ~700 nm.

5.20 EDS spectra obtained from laser patterned sites in (a) Figure 5.20(a) and (b) Figure 5.20(d).

5.21 Graph of ablation threshold (J/cm$^2$) verses thickness (nm) for selectively patterned TiN thin film.

**Chapter 6**

6.1 RBS spectra of TiN on Cr on Si prior to and after etching in SC-1 for 40, 67 and 100 minutes. The spectra indicate that the TiN etched completely from the Cr using SC-1 at a rate of ~6 nm /min. The Cr sacrificial layer is not etched by the SC-1.

6.2 RBS spectra of Cr on Si and after etching in SC-1 for 120 and 390 minutes. The likeness of the spectra indicates that the Cr was not etched in the SC-1 over the time investigated.
6.3 (a) SEM micrograph of partially filtered TiN etched in SC-1 for a period of 40 minutes and (b) EDS spectrum obtained from the highlighted region. The EDS spectrum indicated the presence of TiN.

6.4 (a) SEM micrograph of a partially filtered TiN etched in SC-1 for 63 minutes (b) EDS spectrum indicating the presence of TiN on Cr on Si (c) EDS spectrum indicating the presence of Cr on Si. (Both EDS spectra correspond to the labelled regions in Figure 6.4(a)).

6.5 SEM micrograph of a partially filtered TiN thin film after etching in SC-1 for 67 minutes 40 seconds and a corresponding EDS spectrum indicating the presence of Cr on Si only.

6.6 SEM micrograph of a fractograph of the Cr/TiN/Cr on Si system used to wet-etch TiN thin film.

6.7 RBS spectra of Cr/TiN/Cr on Si prior to and after etching in CEP-200 for 15 and 30 minutes. The spectra show that the Cr contact mask was etched from the TiN and that the TiN was not etched by the CEP-200 over the period investigated.

6.8 (a) SEM micrograph of a wet-etched TiN thin film (20 μm feature) on Cr with the Cr contact mask over the patterned TiN and (b) EDS spectrum indicating the presence of the exposed Cr sacrificial layer.

6.9 SEM micrographs of wet-etch patterned TiN thin film features that underwent etching in CEP-200 to remove the Cr contact mask layer, with feature sizes (a) 20 μμ and (b) 15 μμ (c) 5 μμ and (d) 2.5 μμ.

6.10 EDS spectrum obtained from the region of the etched Cr sacrificial layer indicating that the Cr sacrificial layer was not completely removed.

6.11 SEM micrographs of a laser patterned TiN bridge (length: 76 μm) showing (a) the entire feature and (b) the bottom bridge support.

6.12 EDS spectra obtained from highlighted regions shown in figure 10 (b). The spectra are of areas with the (a) Cr sacrificial layer and (b) TiN only.

6.13 SEM micrographs of a laser patterned TiN bridge (length: 82 μm) showing (a) the entire length of the bridge and (b) a broken section where the bridge joins the support.
Chapter 7

7.1 SEM micrographs of TiN thin films deposited using cathodic arc evaporation with different modes of filtering (a) partially filtered TiN and (b) fully filtered TiN. The micrographs show that the number of macroparticles per area is greater for the partially filtered TiN than the fully filtered TiN.

7.2 XRD spectra of partially filtered and fully filtered TiN thin films deposited at 200ºC showing (a) partially filtered TiN with a (111) preferred orientation and (b) fully filtered TiN with a (220) preferred orientation. The dashed lines represent the planar spacing, $d_0$, for the TiN (111) and (220) orientations in a stress-free state.

7.3 XRD spectra of partially filtered TiN deposited at room temperature and 200ºC. Both spectra show the TiN with (111) preferred orientation.

7.4 SEM micrographs of deformed TiN cantilevers.

7.5 Schematic showing an in-plane view of a cantilever (a) restricted in the z-axis and (b) deflected approximately 50 µm downwards.
List of Tables

Chapter 2

2.1 Types of excimer laser radiation.
2.2 Types of stress structures for measuring stress in thin films.
2.3 Physical properties of TiN.

Chapter 3

3.1 Energies (in keV) of characteristic X-rays of the elements Si, Ti, Cr and Cu.

Chapter 7

7.1 Physical properties of materials.
Chapter 1

Introduction

1.1 MEMS and Integrated Microsystems

MicroElectroMechanical Systems (MEMS) or Microsystems Technology (MST) is the development of functional, sub-millimetre engineering devices, such as sensors and actuators. Being small means that MEMS can be incorporated into our daily lives with minimal impact and with the intention of enabling continuous monitoring and intervention of processes to make them more efficient, cleaner and safer. For example, luxury cars of today are fitted with components fabricated using MEMS technology. These include inertia sensors that initiate the deployment of airbags in the event of an accident, pressure sensors for monitoring tyre pressure and gyratory sensors for vehicle stability. In the near future, it is estimated that MEMS sensors will be used as light detectors for automatic headlight function, water sensors for automatic wiper function, humidity sensors for climate control and so on.

A common objective for MEMS developers is to reduce the size of MEMS. This makes them less obtrusive as engineering devices and more attractive to manufacturers. The reason is because the smaller a MEMS device is the greater the number that can be produced per unit area of workpiece, which reduces the manufacturing cost per device and assists in making the technology more cost competitive. In parallel with this objective is the Holy Grail of MEMS achievements – creation of ‘smart’ devices, i.e., devices that can interpret and process information from their environment and then act to remedy undesirable disturbances. Full realisation of this will only come about through integration of MEMS with Integrated Circuits (ICs), thus encapsulating the sensor, actuator and relevant signal processing circuitry on a single chip.
1.2 Micromachining

The fabrication of MEMS is termed micromachining. MEMS originated from the microelectronics industry and so early advancements in micromachining were centred on the etching of single-crystalline silicon. This technique is referred to as bulk micromachining [1], [2]. The field of micromachining has since expanded to include other techniques such as surface micromachining [3], [4], [5] and LIGA [6]. Each of these three techniques has its own advantages and combining them can create greater flexibility in the realisation of MEMS devices. For example, Hung and coworkers [7] combined surface and bulk micromachining to fabricate a freestanding thermal sensor with a mesh-membrane supporting structure. The thermistor and supporting structure were fabricated using surface micromachining and the undercutting was carried out using bulk micromachining. Other researchers have also used this approach to increase flexibility in their designs [8], [9]. Surface micromachining was central to the work of this thesis and hence some background comments are in order.

1.3 Surface Micromachining

Surface micromachining involves adding planar layers onto a wafer surface, patterning the layers and carrying out a sacrificial etch step to release a functional structure. Surface micromachining offers greater flexibility than bulk micromachining as a wider range of materials can be processed. For example, polymers, glasses, ceramics, metals and alloys are used to serve as either structural, sacrificial or electrical (conductive and insulative) layers [5].

In any surface micromachining strategy, there are three essential processing requirements:

1. Material processing compatibility – materials chosen and their processing methods must be compatible
2. Mechanical integrity between layers – materials chosen must bond to one another and not crack or delaminate during or after the deposition process
3. Etch selectivity – etch selectivity must exist between materials in order for carry out patterning and sacrificial etching.

Consistency of planar fabrication requires patterning structural layers with minimal interference to any sacrificial layers. Likewise, for the sacrificial etch step used to
“release” the structural layer, it is essential that this step does not jeopardise the integrity of the structural (and electrical) layers [5]. The selective removal of the sacrificial layer from the substrate is also highly desirable as it facilitates etching of the Si substrate to further undercut surface micromachined features [7].

It is clear from the above that surface micromachining is a technology offshoot from the manufacture of ICs. Nathanson and coworkers [10] achieved the first surface micromachined structure in 1967 at the Westinghouse Research Laboratory. They fabricated a resonant gate transistor using a gold cantilever beam with a different metal serving as the sacrificial layer. Since that time, the field of surface micromachining has grown and in 1991 Analog released the first commercially available surface micromachined device; the “ADXL50” accelerometer. The ADXL50 was utilised as a motion sensor for airbag deployment [11], [12].

Although the fabrication principles of MEMS and ICs remain similar, it is evident that the physical and mechanical properties of the materials used in the final components of each differ greatly. For example, the structural layer of a surface micromachined motor (micromotor) demands high strength and high wear resistance, whereas the electrical properties of a material are high in importance in IC fabrication. Also, it is crucial that thin films in surface micromachined devices remain planar after the sacrificial release step, which in turn demands that films possess low levels of a type of residual stress known as gradient stress. Gradient stress is the result of a change in stress through the thickness of the film and excessive levels of gradient stress in thin films cause out-of-plane deformation of released structural layers [13]. Typically, such deformation is highly undesirable as it renders devices useless. On the other hand, such issues are less critical in IC materials; so long as the film remains well adhered and has the appropriate electrical properties then it serves its function.

Given the different material requirements between MEMS and ICs, considerable research has been carried out into adapting IC technology for MEMS fabrication. Established IC technologies such as vapor deposition, doping, microlithography and etching techniques have all undergone changes to suit the requirements of MEMS applications. One traditional surface micromachining strategy includes the chemical vapor deposition of polycrystalline silicon (polysilicon) onto a thermally grown silicon dioxide layer, wet-etch patterning the polysilicon with tetramethyl ammonium hydroxide (TMAH) and etching the sacrificial layer of silicon dioxide selectively with
This strategy has undergone various adaptations in order to create better functionality for MEMS applications. These include improvements in chemical vapor deposition (CVD) techniques to produce virtually stress-free films and the doping of silicon dioxide to form phosphosilicate glass (PSG) to enable greater control over the etch selectivity between polysilicon structural layers and PSG sacrificial layers. A plethora of materials can be deposited as thin films. Because materials have their own characteristic properties, there is a constant search for new materials that possess novel properties that can be incorporate into MEMS devices. Introducing a new material typically involves the establishment of a novel material combination i.e., a structural material and a sacrificial layer material that satisfy the requirements of surface micromachining in terms of material processing compatibility, mechanical integrity and etch selectivity.

1.4 Surface Micromachining and Integrated Microsystems

Like IC fabrication, surface micromachining is carried out on the surface of a silicon wafer and therefore is generally considered the most suitable MEMS fabrication technique for the integration of MEMS with ICs. When integrating MEMS and ICs onto a single chip, it is widely thought that the ICs should be fabricated first. This ensures the IC portion of the chip is protected by the more robust MEMS portion. One important limitation with this strategy is that exposing ICs to temperatures over 500ºC is undesirable as thermal diffusion can occur causing irreversible damage to the designed circuitry. In surface micromachining, temperatures greater than 500ºC are commonly used in thin film deposition and in furnaces used to carry out a post-process thermal anneal. In order to introduce a novel thin film material to surface micromachining that has the possibility of being incorporated into a MEMS/IC integrated smart chip, it is essential that the film can be deposited and patterned within the temperature limitation imposed by the IC processing strategy.

1.5 Motivation for TiN

TiN is an advanced ceramic material, which has properties that can be exploited in a wide range of applications. For example, its high hardness has been exploited in many tribological applications; due to being CMOS compatible it has been used as a diffusion barrier in microelectronics [14]; its antireflective behaviour has been seen it used in solar cell
and photolithography applications [15]; due to TiN possessing an aesthetically pleasing golden appearance it has been applied as a decorative coating. Perhaps the main industrial use of TiN to date has been the cutting tool industry, where it provides a hard wear resistant coating on tools such as drills, taps, etc. However, it has the potential to be used for surface micromachined sensors and actuators in many MEMS applications because of its CMOS compatibility and outstanding mechanical properties. Consequently, TiN was chosen for investigation in this study.

In order for TiN to be realised as a suitable MEMS material it is crucial that TiN thin films can be deposited and patterned using techniques that facilitate integration with ICs to form a smart device. As a result, the selection of TiN in the present context will only be feasible provided films can be applied within the temperature limitation imposed by the IC processing technology. TiN is deposited using both physical vapor deposition (PVD) and CVD. The advantage of PVD TiN thin film is that it can be deposited at temperatures below 450°C [16], which is within the temperature limitation imposed by the IC processing technology, whereas CVD TiN is deposited at temperatures around 1000°C. One method of depositing high quality TiN thin films is by using plasma-assisted cathodic arc evaporation. This work presents the patterning of TiN thin films, prepared by cathodic arc evaporation, using techniques of excimer laser micromachining and photolithographic wet-etching. Furthermore, it is well known that TiN deposited using PVD techniques possesses high levels of residual stress [17]. Therefore, in order to determine the effect that residual stress may have on surface micromachined TiN structures, stress-measuring structures were fabricated and released.
Chapter 2

Literature Review

To date, little has been published on the use of TiN for surface micromachined MEMS in comparison to its use on cutting tools. However, the strong interest in TiN means that a significant amount of literature has been published on TiN processing which is of considerable value to potential surface micromachining applications.

2.1 Thin Film Deposition

There exists a variety of ways to deposit thin films for surface micromachining. These include CVD, PVD, Sol Gel and electroplating [17]. With respect to vapor deposition and its exploitation in surface micromachining, materials research and commercial use has focused on CVD, although the use of PVD in surface micromachining has grown in recent years, especially where multi-component materials are desired such as in shape memory alloy (SMA) [18], piezoelectric [19] and magnetic [20] thin films applications.

2.1.1 Chemical Vapor Deposition

Chemical vapor deposition generally involves the high temperature reduction or decomposition of a chemical vapor precursor that contains the material to be deposited. Chemical vapor deposition has been used to deposit TiN by the following reaction [21];

\[
\text{TiCl}_4 + 2\text{H}_2 + \frac{1}{2} \text{N}_2 \rightarrow \text{TiN} + 4\text{HCl} 
\]

Temperatures of over 1000°C are typically used to deposit the TiN. The requirement of high temperature deposition limits the use of CVD processing for MEMS/IC
integration. A variation of CVD that enables the deposition of films at temperature ranging from 25 – 300ºC and is favourable for MEMS/IC processing is plasma enhanced CVD or PECVD [22]. In PECVD, plasma is generated to activate and partially decompose highly volatile organic precursors [23]. Issues that reduce the attractiveness of CVD processes are the need for extremely hazardous precursor gases and the disposal of reaction by-products and unused precursor gases. These factors raise issues about safety and environmental sensitivity [21].

2.1.2 Plasma and Plasma Processing

Plasma is a quasi-neutral gaseous environment that has enough ions and electrons to be electrically conductive. The charged particles are free to move in random directions. Plasma processing is the term given to a process where the plasma is central to the process. The main types of process plasma are continuous DC, Pulsed DC, AC, RF and arc plasma [23]. Process plasmas in surface micromachining can be used to clean substrates, deposit films and etch materials.

2.1.2.1 DC Diode Discharge

The cold cathode DC diode discharge operates in the abnormal glow discharge region where the cathode current density depends on the applied voltage. Figure 2.1 is a schematic of a DC diode configuration and the potential drop across the interelectrode space. Figure 2.1(a) shows the cathode and the cathode dark space, the anode (possible substrate position) and the plasma or glow discharge region. Figure 2.1(b) shows the plasma potential with respect to ground. The voltage drop is high close to the surface of the cathode; referred to as the cathode fall region. The potential across the plasma with respect to ground is very low. This is because the plasma is conductive and close to the anode surface a sheath potential is present. In the DC diode discharge, the cathode attracts ions from the edge of the plasma. These ions accelerate across the cathode fall (normal to the electric field) and impinge on the cathode surface. The large change in potential across the cathode fall induces a strong electric field. The field causes electrons to accelerate rapidly away from the cathode surface whilst also causing ions to accelerate toward the cathode. The presence of fast moving electrons, ions and energetic neutrals results in charge exchange collisions that cause ions and energetic neutrals to impinge on the cathode surface. This impingement on the surface causes the ejection of
secondary electrons, which are accelerated back across the cathode fall and collide with neutrals to generate ions. Hence, at equilibrium, the plasma is self-sustaining [24].

Figure 2.1 Schematic of (a) DC diode discharge and (b) DC potential distribution across the DC diode discharge. From [23].

2.1.3 Physical Vapor Deposition

Physical vapor deposition refers to the process in which atoms are removed from a material into the vapor phase, transported through a low pressure gaseous environment or plasma and condensed or deposited onto the surface of the substrate [23]. The term PVD encompasses a variety of thin film deposition techniques, each of which employs different methods of vapor generation based on either evaporation or sputtering. In PVD processes, the target material or cathode needs to be solid under vacuum and electrically conductive in cases where arc evaporation, e-beam evaporation and DC sputtering are employed. Unlike CVD, PVD processes do not require toxic precursor species and do not produce hazardous by-products. This means PVD processes are cleaner and safer. It is considered [25] that one of the limitations of PVD films is that they have columnar grain growth. Columnar growth occurs when the mobility of depositing atom is limited. Columnar structure affects the mechanical properties of thin films by reducing the fracture toughness and making them prone to cracking [26]. Hence, most PVD processes provide some form of ion assistance (i.e., ion-bombardment) by substrate biasing which leads to the development of much finer microstructure.
2.1.3.1 Sputtering

Sputter deposition involves the impact of high-energy particles onto the surface of a target material. The use of plasma to generate the high-energy particles is the most common method (see section 2.1.2.1). The sputtering process occurs when the ions and energetic neutrals that impinge on the cathode have sufficient energy to dislodge atoms (and ions) from the target surface into a vapor state. The removal of target material is governed by momentum transfer and is made possible when the kinetic energy of an impinging species is sufficient to overcome the binding energy of the target material. Typically, the sputtering process uses argon as the ion source (Ar⁺). Sputtering a metallic target in an argon atmosphere allows the deposition of metallic films. The addition of reactive gases such as O₂ or N₂ enables compounds such as metal oxides and metal nitrides to be deposited. The procedure is then referred to as reactive sputtering.

DC sputtering is a common method for depositing films. It is essential in DC sputtering that the target material is electrically conductive. If the target is not sufficiently conductive then a positive charge builds up at the cathode surface and sputtering ceases to occur. RF sputtering can be used to overcome this problem as it enables dielectric targets to be sputtered.

In a further development of sputtering, known as magnetron sputtering, magnets are placed behind the target resulting in a denser plasma above the target, which in turn improves the efficiency of sputtering.

De Moor and coworkers [27] used reactive sputtering to deposit combined Ti/TiN thin films for microheaters. The Ti was deposited to act as an adhesion layer to the silicon dioxide layer. No further information about the deposition was provided.
2.1.3.2 Cathodic Arc Evaporation

Cathodic arc evaporation utilises a high current, low voltage arc to vaporise a cathodic electrode and deposit the vaporised material on a substrate [23]. The arc is initiated on the cathode surface to form a “cathode spot” that has a current density of 10^6-10^8 A/cm^2 [25]. The arc travels rapidly across the surface of the cathode in a random manner and erodes the cathode material by melting and vaporisation [23]. The emitted material consists of ions, electrons, neutrals and macroparticles. The arc ionises the vaporised material, generating self-sustaining plasma [23]. One major requirement is that the cathode be electrically conductive.

The introduction of gases into the vacuum chamber facilitates the deposition of compounds and provides assistance in the stability of the arc. In the case of reactive deposition, reactive gases such as N\textsubscript{2} and O\textsubscript{2} provide for the deposition of nitrides and oxides respectively. Metallic films are typically deposited in an argon atmosphere.

The distinct feature of cathodic arc evaporation is the high degree of ionisation of the arc plasma. Martin and coworkers [28] reported that the ion content in Ti arc plasma could be as high as 70-80 %. Another distinct feature of cathodic arc evaporation is the high energy of the particles. It has been reported that Ti ions reach peak energies of around 40-50 eV. This is significantly higher than thermal evaporation based deposition methods that have energies of around 0.1-0.5 eV per particle and sputtering which is in the order of 5 eV [28]. Due to the high degree of ionisation of the arc plasma, applying a negative bias to the substrate can increase the energy of the depositing species. Increasing the energy has been reported to reduce the stress in TiN thin films and increase the adhesion of the film to the substrate through the process of ion bombardment [29].

It is possible to deposit a variety of materials by cathodic arc evaporation by selecting the composition of the cathode material and the reactive gas added to the chamber. Metals and alloys, nitrides, carbides, carbonitrides, oxides and diamond-like-carbon (DLC) have been deposited using cathodic arc evaporation [25]. This technique has also been used to deposit Cu for the metallisation of trenches and vias in microelectronic structures [30].

One of the problems with films deposited by cathodic arc evaporation is the presence of macroparticles. Macroparticles are essentially solid particles explosively emitted from the target material [31]. Macroparticles can be up to tens of micrometres in diameter.
and can be deposited throughout any stage of the film growth process. The presence of such large particles degrades thin films and limits their potential use in microelectronics and precision optics [25]. Considerable effort has been expended in reducing the presence of macroparticles in films. Increasing the cathode spot velocity by magnetic fields or by fast rotation of the cathode has been reported to markedly reduce macroparticle emission [30]. Another way is to physically filter the plasma stream.

2.1.3.3 Filtered Arc Deposition

The presence of macroparticles can be significantly reduced or even eliminated by physically filtering plasma [32]. Such a system is referred to as a filtered arc deposition system (FADS). Filtering of TiN thin films, in particular, has received considerable interest and this has led to the successful deposition of particle free coatings with considerable improvement in the wear resistance and other mechanical properties of the films [33]. There exist many different types of filters. The most common types are described in the following two paragraphs, however for a more thorough overview of the types of filters see source review articles by Martin and Bendavid [25], and Karpov [34].

The most elementary method of macroparticle removal is by physically shielding the substrate in a technique known as simple shielding. A shield is placed in front of the substrate to block macroparticles. Film ions are attracted around the shield by applying a bias to the substrate. The main drawback with simple shielding is a vastly reduced deposition rate. The Venetian Blind filter is one technique that works on a similar principle to simple shielding but has the advantage of not suffering the large decrease in deposition rate. This technique employs a series of angled plates that block macroparticles [25].

A more effective method for eliminating macroparticles is to control the plasma using applied magnetic fields. An electric field may exist in arc plasma if a magnetic field is applied. The magnetic field lines are equipotential lines of the electric field. Therefore, it is possible to control the electric field structure and the arc plasma flow motion by means of the magnetic field [34]. The application of a magnetic field induces the acceleration of electrons through the field. In order to balance charge, positive ions are attracted to the electrons and in doing so are accelerated. The strength of the magnetic field is governed by the energy required for electron acceleration not direct ion
acceleration – the ions have far greater mass to be affected by the magnetic field. The net effect is that the magnetic field increases the density of the plasma. This means the ratio of ions to macroparticles is increased and in turn the deposition rate is increased and for a given film thickness the exposure time of the substrate to macroparticles is decreased, and therefore the number of macroparticles being deposited on the surface is decreased. Macroparticle filtering of this type is carried out using a linear filter and is termed linear filtering or partially filtering. Using magnetic fields in the form of plasma ducts can be used to filter practically all the macroparticles. This is achieved by offsetting the source duct and applying a magnetic field to induce the ions to move around a bend. In this case, the ions follow the electrons around a bend, whereas the neutrals and macroparticles travel straight and deposit onto the wall of the filter duct. This method of magnetic filtering is categorised as fully filtering and the most common types of magnetic filters to achieve this are toroidal (various), ‘S’-shape (various) and the knee-bend [25]. A more detailed description of filtered arc deposition in covered in section 3.3.

2.1.4 Pulsed Laser Deposition

Pulsed laser deposition (PLD) is a technique used to deposit thin films. Pulsed lasers such as the Nd:YAG, excimer and Ti:sapphire lasers have been used to ablate a target material in a low pressure environment. The ablation process forms a plume of partially ionised material (plasma plume) above the ablation site. The ablated material deposits onto a substrate to form a thin film. The advantage of PLD is that the composition of the deposited material is extremely close to that of the target material. This enables the deposition of complex materials that rely on an exact stoichiometric ratio. One example is the deposition of high temperature superconductor thin films of YBa$_2$Cu$_3$O$_{7-x}$, in which case the target material is hot isostatically pressed [17].

Several researchers have used excimer lasers to ablate bulk TiN targets and deposit TiN thin films. Auciello and coworkers [35] laser ablated a TiN target in a vacuum chamber using an ArF excimer laser ($\lambda = 193$ nm, PRF=100 Hz, $\tau = 40$ ns), whereas Wang and coworkers [36] laser ablated a TiN target (99.9% purity) in a vacuum chamber using a KrF excimer laser and pulse duration of 23 ns. In their work, neither discusses the ablation behaviour of the TiN.
2.2 Microlithographic Etching

Lithography utilises an etch resistant mask in order to produce a patterned relief that is created by etching exposed material. When the technique is applied to produce micrometer scaled features it is termed microlithography. Microlithography has been used industrially in the fabrication of microelectronic circuits since the mid-20th century. Today, it is also used for patterning thin films for surface micromachining. In microelectronics, patterning resolutions of about 0.01 μm are possible using electron-beam lithography, however, in surface micromachining resolution requirements are less stringent and are acceptable at around 0.5 μm. Fabricating microstructures using microlithography involves preparing an etch resistant mask on the surface of the work piece. This is achieved by exposing a resist to a suitable source of energy (e.g., electron-beam, UV light) and developing it in a suitable developer. The mask pattern may be either a positive or a negative version of the exposure radiation, a choice that is dependent on whether the resist is a positive or negative tone resist. There exist several energy sources used in microlithography. Each source varies in resolution and the resolution can also vary between equipment types as well [37]. Figure 2.2 shows a chart detailing potential new high-resolution lithography tools and their corresponding minimum linewidth dimensions [38].

Figure 2.2 Potential new high-resolution lithography tools. From [38].

Extreme UV (EUV) is potentially a method of choice for surface micromachining, however currently the most common method is UV photolithography despite having resolution of around 0.5 μm. The technique uses UV or visible light and an imaging system to expose the photoresist. Its popularity is due to its high throughput capability, ease of use and low capital cost compared to the other techniques. Mask aligners and steppers are the most common imaging systems. The main drawback of UV photolithography is that it is labour intensive. Preparing a resist mask takes around 20-30 minutes and involves spin coating, baking, exposure, development and rinsing. Once the resist is prepared, etching can ensue, with the final step being the complete removal of the resist.
2.2.1 Wet-etching

Wet-etching is the process of removing material under the action of a liquid. Wet-etching can be used to remove semiconductor materials, polymers, ceramics, metals and alloys.

There exist a variety of TiN etching solutions reported in the literature [39], [40]. One of these is SC-1 (Standard Clean 1). SC-1 was developed as a silicon wafer cleaning solution by W. Kern and D. Puotinen in 1965 and disclosed in 1970. SC-1 is also known as Ammonium Hydroxide Peroxide Mixture (APM) and consists of a solution of hydrogen peroxide and ammonium hydroxide. SC-1 is also known to etch SiO$_2$, Si$_3$N$_4$, Si and Ti [41]. The etch characteristics of TiN in SC-1 have been investigated by various researchers [41], [42], [43]. Within these investigations, the role of H$_2$O$_2$, OH$^-$ and OH$_2^-$ was the focus. Philipossian and Magana [43] investigated the stability of the SC-1 in TiN etching over time. By assuming a two-step etching mechanism, whereby the Ti is first oxidised by the H$_2$O$_2$ and then the product is then dissolved in the alkaline solution, they showed that the oxidation rate of the Ti with H$_2$O$_2$ is the rate-limiting step, rather than the dissolution of the TiO$_x$. They reported that the latter step was discounted as the rate-limiting step due to the NH$_4$OH concentration having a minor effect on the TiN etch rate. They observed that a two-fold increase in the H$_2$O$_2$ concentration corresponded to a four-fold increase in the TiN etch rate from 3 to 12 nm/min. In contrast, Verhaverbeke and Parker [41] developed a theoretical model for the etching of TiN in SC-1 solutions and found that etching TiN in SC-1 follows a first order reaction with OH$_2^-$, meaning that H$_2$O$_2$ is not the primary oxidant in the reaction. They state that NH$_4$OH is an important addition to the solution as it substantially increases the OH$_2^-$ concentration, which increases the etch rate. Furthermore, they reported that the etch rate is dependant on the temperature through the consideration of two factors; the activation energy increases the etch rate over the temperature range but the peroxide anion concentration decreases with temperature, however the activation energy is the dominant factor.

Alekseev and coworkers [44] reported the development of the TiN film etching solution that contains sulphuric acid for removing TiN from plain carbon, tool and stainless steels. They report an etch rate of 185 nm/min and state that the solution should be used in the temperature range 18-24°C.
TiN is also etched in HF acid. Witvrouw and coworkers [45] investigated the etch rate of TiN using sheet resistance measurements when etched in HF acid and Buffered HF (BHF)/glycerol. They reported an etch rate of 0.4 ± 0.2 nm/min in 24.5 % HF (in DI water) and an etch rate of 0.06 ± 0.05 nm/min in BHF/glycerol. Using the analytical technique of Auger depth profiling, they found that etching TiN with HF acid produces a Ti-oxide layer on the surface of the film, which increased the resistivity of the surface and inhibited the ability to measure the etch rate of the TiN film with any accuracy. Because of this inaccuracy they concluded that their measurements can only be taken as an estimation as they reflect the change in resistivity more so than the etch rate. Much of the published work deals with the use of etchants to remove TiN, however, there is little work reported on which TiN is patterned using wet-etching.

2.2.2 Dry Etching

Dry etching is the removal of material through sublimation using a gaseous medium. Dry etching encompasses a variety of techniques of which reactive ion etching (RIE), plasma etching and gas-phase etching are most common. Plasma etching to pattern a material uses the identical material removal process that is used when sputtering a target material in sputter deposition (see section 2.1.2.1). Plasma etching is carried out in RF generated plasma inside a low-pressure chamber. RF power is employed so that insulative materials can be etched and polymeric photoresists can be used as masks. A parametric guide to plasma etching TiN in an Ar atmosphere is presented in [40].

The process of RIE takes place in plasma, whereby material is removed by reactive ion species and enhanced by ion bombardment of the substrate [24]. Some common species used in RIE are O₂, SF₆, CF₄, Cl₂ and BCl₃ [46].

Hilleringmann and coworkers [47] investigated the patterning of MOS type materials including TiN at line widths of 100 nm or below using RIE. The TiN was deposited using CVD. They used pure SiCl₄ to etch the TiN and stated that the selectivity to SiO₂ is high. Line widths down to 80 nm were reported. They stated that structure widening occurred when etching in pure SiCl₄ and to suppress this effect a small amount of chlorine was added to the plasma. Loong and Chiu [15] investigated the photolithographic patterning of Al/Si metallisation systems with TiN deposited over the Al/Si to serve as an antireflection layer, i.e., TiN/Al/Si. They reported that patterning
was carried out using RIE and that TiN was selectively etched from Al using a gas mixture of 3:7 CHF₃:CF₄ with a DC bias of -100 V. De Moor and coworkers [27] patterned Ti/TiN heater coils using a standard RIE process. No further details of the etching process were given.

Gas phase etching with XeF₂ and HF is commonly used in surface micromachining [48]. XeF₂ etches Si readily, whereas SiO₂, photoresists and aluminium are not attacked [49]. HF readily etches SiO₂ and native silicon oxides but alone does not etch Si. Köhler [37] provides detailed descriptions of three Si etching solutions that contain HF. The most common Si etchant that contains HF is an isotropic etchant known as HNA. HNA contains HF, HNO₃ and CH₃OOH (acetic acid) and has many variations that depend on the concentration of each acid. It is commonly thought that the removal of Si with HNA occurs through a two-step process whereby the Si is oxidised by HNO₃ and the SiO₂ is then etched by the HF [11]. Witvrouw and coworkers [45] investigated the etching of TiN in HF and reported an etch rate of 0.06 ± 0.02 nm/min at 35°C.

### 2.3 Laser Micromachining

Patterning films using photolithography requires labour-intensive processing steps. One method for reducing the number of steps is to pattern films using a laser. To act in accordance with surface micromachining requirements, the laser should completely remove the film with minimal thermal impact on the surrounding region [50], i.e., sacrificial layers, the substrate and adjacent film zones. This can be achieved by keeping the irradiation time to a minimum, as the amount of heat accumulated in the substrate is proportional to the irradiation time (assuming constant heat loss). Lasers emit radiation in either continuous wave (CW) or pulsed mode. The irradiation time of a CW laser can be controlled using fast beam motion, where the effective time of action is expressed as \( \tau_{\text{CW}} = v.d \) (\( v \) is the beam speed and \( d \) is the beam diameter). The demands of thin film processing are stringent and the level of control available in CW laser processing is typically insufficient. Pulsed radiation is more suitable than CW radiation for patterning films as a short duration of radiation, referred to as a pulse, enables material removal with less heating of the substrate [51].

Broadly speaking, materials can be broken into two classes; thermal insulators and thermal conductors. For thermal insulators, the optical absorption depth dominates pulsed laser ablation;
where $\alpha$ is the optical absorption coefficient (cm$^{-1}$), and is material and wavelength dependant. When a laser pulse impinges on the surface of a thermal insulator, such as a polymer, the radiation penetrates the material according to a simple relationship known as Beer’s Law;

$$ I_t = I_0 \cdot 10^{-\alpha d} $$

(3)

where $I_0$ and $I_t$ are the intensities of the laser beam prior to and after transmission through a slice of material of thickness $l$, and $\alpha$ is the optical absorption coefficient of the material [52]. Figure 2.3 shows a schematic representation of laser irradiation and ablation of a polymer. If the fluence, $F$, or energy density of the laser beam is above the ablation threshold, $F_0$, of the material, then a depth $l_f$ of the material will be ablated by the pulse. The next pulse will ablate virgin material and so on.

Figure 2.3 Schematic representation of the laser irradiation and ablation of a polymer. From [52].

Experiments have shown that below the threshold fluence, all the absorbed energy appears as heat. Above the ablation threshold, the etch depth per pulse or etch rate, $l_f$, can be approximated by [52];

$$ l_f = \frac{1}{\alpha} \ln \left( \frac{F}{F_0} \right) $$

(4)

For thermal conductors such as metals, alloys and nitrides, ablation is dominated by thermal induced effects of the heat-affected-zone (HAZ). The depth of the HAZ is
dependant on the material properties and the pulsewidth of the laser, and is expressed in terms of the thermal length;

\[ L_{th} = 2\sqrt{D\tau} \]  \hspace{1cm} (5)

where \( D \) is the thermal diffusivity (cm\(^2\)/s) and \( \tau \) is the pulsewidth (s). The thermal diffusivity is fixed for a given material and is expressed as;

\[ D = \frac{k}{C_p \rho} \]  \hspace{1cm} (6)

where \( k \) is the thermal conductivity (J.(s.m.K\(^{-1}\)), \( C_p \) is the specific heat capacity (J.(K.kg\(^{-1}\)) and \( \rho \) is the density (kg.m\(^{-3}\)) [53].

In view of these principles, it should be possible to selectively laser ablate a thermal conducting thin film in a single pulse providing the film thickness is similar to \( L_{th} \). The pulsewidth of lasers depends on the type of laser and its mode of operation. There exist a variety of pulsed lasers used to micromachine thin films.
2.3.1 Nd:YAG

The Nd:YAG is the most commonly used laser in microengineering. Nd:YAG lasers are focused beam lasers that can be operated at frequencies up to 10 kHz in the UV to IR spectral range. The fundamental wavelength is 1064 nm. Multiplying the frequency of the crystal to the second, third and forth harmonics enables operation at wavelengths of 532 nm, 355 nm and 266 nm respectively. Nd:YAG lasers have been used to micromachine a wide variety of materials, including metals, semiconductors, ceramics, polymers and glasses [54]. Commercially, the Nd:YAG laser has become a popular choice for applications such as drilling, cutting materials (in thin sheet form), welding and trimming circuits.

In an investigation related to tooling, Kononenko and coworkers [55] used a Nd:YAG and a Nd:YAP laser to ablate craters into the surface of 1 µm thick TiN films deposited onto steel (AISI 440C) substrates. The main requisites of their work were that crater depths were to be less than the thickness of the film and that the ablation process should not crack or degrade the mechanical strength of the film or decrease the adhesion between the film and the substrate. A decrease in adhesion between a film and substrate will make a film more susceptible to delamination. Indeed, they reported the complete removal of the TiN film from the substrate when ablated with more than a single 150 ns pulse at a wavelength of 1064 nm. They stated the removal process was caused by heating (or even melting) of the substrate and degradation of the film/substrate adhesion. The penetration of thermal energy through to the substrate was made possible as the depth of the HAZ (using equation (5)) of a 150 ns pulse equates to 2 µm (where \( D = 0.065 \text{ cm}^2/\text{s} \) for TiN [55]), which is greater than the thickness of the TiN film.

Bonse and coworkers [56] micromachined a 3.2 µm TiN film using an externally frequency-doubled Nd:YAG laser (\( \lambda = 532 \text{ nm} \)) with a single pulse at a fluence of \( \sim 22 \text{ J/cm}^2 \). The TiN was deposited on single crystal silicon and was observed to have a (200) orientation. The pulsewidth of the laser was 9 ns, which equates to a HAZ depth of approximately 480 nm. They reported that the TiN film was not completely removed, however laser-induced cracking and bubble formation was observed on the surface of the film.
2.3.2 Ti:sapphire

Like Nd:YAG lasers, Ti:sapphire femtosecond pulsed lasers are focused beam lasers. The advantage of using a femtosecond-pulse laser is that a reduction in the pulsewidth limits the thermal diffusion into the peripheries during the ablation process and increases the quality of the laser machining. Ti:sapphire lasers have been used to micromachine a variety of materials including metals, ceramics and dielectrics. They have the potential to be use for commercial applications and have been demonstrated in the areas of fabrication of injection nozzles, medical implants (stents) and biosensors. Indeed, some laser systems have already been installed particularly for mask repair in industry [56].

The Ti:sapphire laser has also been used to micromachine TiN films [56], [57], [58], [59], [60]. Bonse and coworkers [58] used a Ti:sapphire laser ($\lambda = 800$ nm, $\tau = 130$ fs, PRF = 2 Hz) with a linearly polarised beam to micromachine a 3.2 $\mu$m thick TiN film. At a thickness of 3.2 $\mu$m, the TiN film can be considered to behave as bulk TiN. This is because the ablation process is dominated by the optical absorption depth, which was reported by the authors to be 23 nm. Furthermore, the dominance of the optical absorption depth is due to the thermal length being less than 1 nm. They reported the single pulse ablation threshold of the TiN to be 0.26 J/cm$^2$. They also reported perforating the TiN film through to the silicon substrate using 100 pulses at a fluence of 3.8 J/cm$^2$. The beam ablated the underlying silicon substrate and formed columnar structures. In a parallel publication, Bonse and coworkers [56] ablated the same thickness TiN film (3.2 $\mu$m) under the same conditions, except that in some experiments the beam was polarised circularly using a zero-order quarter-wave plate. They reported the perforation of the TiN film through to the silicon substrate using 50 pulses at a fluence of 3.0 J/cm$^2$ for the circularly polarised beam and 80-90 pulses at a fluence of 1.06 J/cm$^2$ for the linearly polarised beam. In these cases, the silicon substrate was ablated and formed columns in the centre of the irradiated site. Since the precision of the ablation of the interfacial region between the film and the substrate was a major focus of the paper, they compared the roughness of ablated cavities using atomic force microscopy (AFM) when ablated at a fluence of 0.43 J/cm$^2$ under the two beam polarisation modes. The results showed that the roughness of the ablated cavities reduced by a factor of 2-3 when ablated with the circularly polarised beam over the linearly polarised beam. In the pursuit of a micromachining process, this is considered a
favourable outcome, and one that will enable the patterning and complete removal of TiN thin with minimal impact on the underlying material.

Dumitru and coworkers [57] laser ablated a TiN film using a Ti:sapphire laser. The TiN was deposited on steel substrates to a thickness of 1 μm using a CVD system. The pulsewidth of the incident beam was 150 fs, while the PRF was $10^4$ Hz. They reported that the TiN film was penetrated using 8-9 pulses and that subsequent pulses induced ablation of the steel substrate. They reported the single pulse ablation threshold fluence of the TiN to be 0.3 J/cm$^2$. This is similar to the 0.26 J/cm$^2$ determined by Bonse and coworkers [58].

2.3.3 Excimer Laser

The excimer laser is the most commonly used laser for applications requiring high energy UV radiation. Excimer laser radiation is generated by the rapid decay of molecules that have a high inversion from a thermally unstable ground state to excited states. The molecules are rare gas and halogen combinations $RgX$ ($Rg = Ar, Kr, Xe$ ; $X = F, Cl$), which are bonded under high pressure and electrical discharge. The reaction is as follows:

$$Rg^+ + X^- \rightarrow RgX^+ + M; M = He,Ne$$

(7)

He and Ne are used as buffer gases [61]. Depending on the gases used the wavelength of excimer laser radiation ranges from 157 – 351 nm. Table 2.1 lists the gas types and corresponding wavelengths.
Table 2.1 Types of excimer laser radiation.

<table>
<thead>
<tr>
<th>Gas Types</th>
<th>F₂</th>
<th>ArF</th>
<th>KrCl</th>
<th>KrF</th>
<th>XeCl</th>
<th>XeF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength (nm)</td>
<td>157</td>
<td>193</td>
<td>222</td>
<td>248</td>
<td>308</td>
<td>351</td>
</tr>
</tbody>
</table>

The most productive wavelengths for the purpose of direct ablative micromachining are 308 nm, 248 nm and 193 nm. Unlike Nd:YAG and Ti:sapphire laser systems, the excimer laser micromachining system uses mask projection as a means of patterning. This means it is capable of ablating features with spatial resolutions around 1 μm or better. In addition, excimer lasers have a depth resolution in the order of 0.1 μm.

The excimer laser has been used to micromachine various materials including polymers [62], [52], ceramics [63], [64] silicon [62], metallic thin films [65], [66], [67], [68], [69] [70], [71], and ceramic thin films including ZnS [72], WC [73] and TiN [73], [74], [75], [76].

Schubert and coworkers [73] used excimer laser radiation to remove TiN films from coated drills. The aim of their study was to completely remove the TiN with no significant increase in roughness of the underlying surface, as compared to the pre-coating roughness, and in minimal processing time. The TiN films were deposited onto steel drill bits to a thickness of 3 μm using a standard PVD technique. The TiN was ablated under the following conditions; λ = 248 and 308 nm, τ = 23-100 ns, fluence = 1-10 J/cm². They reported the complete removal of the TiN, with an acceptable increase in roughness of the substrate, using an optimised process and 4-20 pulses.

2.3.4 Pulsed Laser Ablation

A requirement in surface micromachining is that structural layers be patterned selectively from sacrificial layers. In addition, damage to the sacrificial layer should be kept at a minimum. Patterning a thin film within these limitations using an excimer laser requires precise pulsed laser ablation conditions and knowledge of the physical and optical properties of the material. For instance, TiN is considered a thermal conductor as it has a higher thermal conductivity than Ti. This means that the heat-affected-zone
(HAZ), as opposed to any photochemical effect, plays the dominant role in the ablation process. Subsequently, control over the HAZ will ensure that damage to the sacrificial layer is minimised; see equation (5).

The exact role of the HAZ on the ablation process of thin films is still subject to continued research. According to measurements conducted by Kononenko and coworkers [55], the optical absorption coefficient of TiN only weakly depends on the wavelength in a wide UV-IR spectral range. They calculated the optical absorption length to be in the range of 25-35 nm for the first, second and fourth Nd:YAP laser harmonics. Since the wavelength of the fourth Nd:YAP laser harmonic of 270 nm is located close to the excimer laser wavelength of 248 nm, it has been assumed that the calculated range can be applied to this work. Therefore, the influence of the laser pulsewidth on the HAZ thickness and, finally, on the ablation process is significantly more important. If we consider the pulsewidth of the excimer laser used in this study, $\lambda = 20$ ns, and the TiN thermal diffusivity, $D = 0.065$ cm$^2$/s, then by equation (5) the HAZ is calculated to be 720 nm.

### 2.3.5 Thin Film Ablation Mechanisms

To date, three basic mechanisms have been proposed for thin film ablation, namely, pure vaporisation of the thin film material [50], solid phase explosive removal, caused by a pressure build-up at film/substrate interface as a result from substrate vaporisation [77] and two-phase removal, which is characterised by partial vaporisation and subsequent pressure induced liquid expulsion [78]. In a recent investigation, Tóth and coworkers [66] found that thin metal film ablation could not be categorised as a single mechanism, but rather a combination of the following processes: film vaporisation, liquid expulsion caused by gas formation and subsequent pressure build-up at the film/substrate interface, and thermal induced stresses which can induce film exfoliation.

### 2.3.6 Selective Laser Micromachining of Thin Film Systems

The laser micromachining of thin film systems with a focus on the selective removal of one film from an underlying film has only been reported on a few occasions. In a study related to microlithography and semiconductor device fabrication, Hunger and coworkers [68] reported the selective removal of a 0.4 $\mu$m thick Al film from a 0.7 $\mu$m thick SiO$_2$ layer on Si using a KrF excimer laser at a fluence of 1.38 J/cm$^2$. By
setting the laser fluence to a value above that of the ablation threshold of Al of \( \leq 0.9 \) J/cm\(^2\) and below that of the ablation threshold of SiO\(_2\) of 1.4 J/cm\(^2\), they reported complete removal of the Al film using several pulses without ablating the SiO\(_2\) layer. They conclude that it may be possible to ablate other metallic films from SiO\(_2\) such as Ni, Au and Cu as they have ablation thresholds of less than 1 J/cm\(^2\), which is below that of SiO\(_2\).

Lecours and coworkers [79] reported using a pulsed Xe laser (\( \lambda = 0.48 – 0.54 \) \( \mu \)m; \( \tau = 1 \) \( \mu \)s; PRF = 30 Hz) with a square spot size of 40 \( \mu \)m \( \times \) 40 \( \mu \)m in a direct writing capacity to selectively ablate thin film materials from one another in the fabrication of a CO\(_2\) thin film electrochemical sensor. They reported three instances of selective laser ablation of one or more thin films from an underlying thin film. It should be noted that the selective removal of the thin films required more than a single pulse per area. With this in mind the three instances are outlined as follows:

1. Selective ablation of a \( \sim 0.3 \) \( \mu \)m thick Pt thin film from a \( \sim 0.3 \) \( \mu \)m thick SiO\(_2\) layer. They reported the ablation threshold for the Pt film was 7.5 J/cm\(^2\) and that using 12.5 J/cm\(^2\) induced unwanted damage to the underlying SiO\(_2\) layer. Optimised conditions of 10 J/cm\(^2\) and a scanning velocity of 500 \( \mu \)m/s were selected. This scanning velocity equated to the Pt film being irradiated with 2.4 laser pulses per area.

2. Selective ablation of a \( \sim 0.5 \) \( \mu \)m thick NASICON (Na Super Ionic Conductor; Na\(_{1-x}\)Zr\(_2\)Si\(_x\)P\(_3\)3-xO\(_{12}\), 0\(<\)x\(<3\) thin film from the above mentioned Pt film without piecing the Pt film. They reported difficulties in this step due to the observed narrow window for NASICON ablation, however reproducibility was achieved by the sputtering of a thin layer of Au or Pt (\( \sim 100 \) nm) over the NASICON. In this instance, an optimised scanning velocity of 100 \( \mu \)m/s was selected. This equated to laser ablating with 12 pulses per area.

3. The final step in the fabrication strategy was to selectively ablate a Na\(_2\)CO\(_3\) thin film from the NASICON film: this was not achieved. The best result achieved was the ablation of both the Na\(_2\)CO\(_3\) and NASICON films together (also with the use of a thin absorbing layer) from the Pt layer without perforation of the Pt layer. An optimised scanning velocity of 100 \( \mu \)m/s was also selected for this processing step.
More recently, Wang [65] reported using a KrF excimer laser (and mask projection system) to pattern SmCo magnetic thin films from Cr thin films deposited on Si wafer and SiO$_2$ coated Si wafer. Wang reported partial removal of a 200 nm thick SmCo film from the underlying Cr film using two pulses at a fluence of 1.29 J/cm$^2$. Energy dispersive spectrometry (EDS) analyses carried out on two laser patterned regions only indicated the presence of Co in one of the obtained spectra. The other spectrum indicated that SmCo had been completely removed. High quality patterning of the SmCo thin films was achieved, however a resolidified boundary rim around laser patterned regions was observed.

2.4 Residual Stress in Thin Films

Residual stress or internal stress occurs in most thin films. It is commonly thought that film cracking, delamination/spallation and void formation are linked to residual stress [80]. Indeed, the deformation of released thin film microstructures is attributed to residual stress [81].

The total residual stress in a thin film can be represented as:

$$\sigma_{\text{total}} = \sigma_{\text{intrinsic}} + \sigma_{\text{extrinsic}}$$  \hspace{1cm} (8)

and can be isotropically quantified by the following equation;

$$\sigma = \frac{E \varepsilon}{(1 - \nu)}$$  \hspace{1cm} (9)

where $E =$ Young’s modulus, $\nu =$ Poisson’s ratio and $\varepsilon =$ strain. The term; $\frac{E}{(1 - \nu)}$ is the biaxial modulus and is preferred in thin film stress measurements as uniaxial testing of thin films is difficult to achieve [82].

Extrinsic stress, $\sigma_{\text{ext}}$, is the result of unintended external factors such as mismatch in thermal coefficient of expansion (TCE) or package induced stresses that may cause uniform plastic deformation. Thermal stresses develop in thin films during the cooling process after deposition at high temperature. Thermal stresses are unavoidable and result from a mismatch in TCE between the film and substrate. Thermal stress is the
most common form of extrinsic stress, is well understood and often easy to calculate. By considering TCE as independent of temperature, the thermal strain can be calculated using the following equation:

\[ \varepsilon_{th} = (\alpha_{\text{film}} - \alpha_{\text{sub}})(T_{\text{depos}} - T_{\text{room}}) \quad (10) \]

Furthermore, the value for the thermal strain can be readily substituted into equation (9) to calculate the thermal stress.

Intrinsic stress, \( \sigma_{\text{int}} \), is a reflection of the internal structure of a material and is known to be caused by internal factors such as lattice mismatch, substitutional or interstitial impurities, the growth processes and phase transformations or volume change stresses [82].

Stresses in thin films are either compressive or tensile. Compressive stress is the result of a negative strain field, which causes the film to expand parallel to the surface and can induce buckling, blistering or delamination in extreme cases. Tensile stress is the result of a positive strain field, which contracts the film parallel to the surface. In extreme cases of where the fracture limit of the material is exceeded, cracking and spallation occurs.

As well as being under compressive or tensile stress, a thin film may have gradient stress. As previously mentioned in Section 1.3, gradient stress is the result of a change in stress through the thickness of the film. Releasing a surface micromachined structure that has gradient stress causes out-of-plane bending of released structures [13]. Gradient stress is typically associated with the film deposition process. It is well known that stress in PVD thin films increases with increasing thickness and one of the main reasons is due to atomic peening of the substrate by the depositing species. Reducing stress in a thin film can be achieved by rearrangement of the atoms, either during the remainder of the deposition or by post-deposition thermal annealing. When a film is annealed, it undergoes densification or expansion and the stresses are reduced [82].

### 2.5 Measuring Stress in Thin Films

Measuring the stress in a thin film is useful for determining the effect that stress could have on a surface micromachined device, including the prediction of effects such as film buckling, bending or cracking.
Chapter 2 Literature Review

There exist a variety of techniques used to measure stress in thin films. In order to quantify any measurements of film stress it is important to consider the type of stress that is being evaluated. Under the general term of thin film stress, there exist three categories:

- **Residual or internal stress** is the stress contributed by intrinsic and extrinsic stress factors.
- **Average stress** in a thin film refers to the stress over a large area, mm to cm range.
- **Local stress** is the stress across a localised region of the film, μm to mm range. Local stress incorporates the contribution by residual stress and external effects (gravity, electrostatic) placed on the film or microstructure.

Typically, residual stress is measured by X-ray diffraction (XRD), average stress is measured using wafer curvature [81] and cantilever plate [83] methods and local stress is measured using micromachined stress measurement structures.

Micromachined stress-measurement structures are *in situ* microstructures that are fabricated to provide a qualitative and quantitative assessment of the local stress in a thin film. The sacrificial release of a thin film structure, which is under stress will result in deformation of the structure that is representative of the stress in the film. The deformation occurs because of the release of strain constraint, whereby the film is free to deform in order to minimise the stress. The stress in the film is determined by measuring the deformation and applying equations that relate the deflection or bending of a structure (strain) to the stress in the film. Stress structures can be used to determine compressive, tensile and gradient stress. A variety of surface micromachined stress structures can be used to measure stress. Table 2.2 lists the types of stress structures for measuring stress in thin films.
Table 2.2 Types of stress structures for measuring stress in thin films.

<table>
<thead>
<tr>
<th>Measurement Technique</th>
<th>Measurable Stress State</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vernier strain gauges</td>
<td>Compressive or tensile stress</td>
<td>[84] [85]</td>
</tr>
<tr>
<td>Curling beam cantilevers</td>
<td>Gradient</td>
<td>[85] [86] [87] [88] [89] [90] [91] [92] [93]</td>
</tr>
<tr>
<td>Fixed-fixed beams or bridges</td>
<td>Uniaxial compressive</td>
<td>[13] [81] [85] [86] [91] [94] [95]</td>
</tr>
<tr>
<td>Diamonds</td>
<td>Uniaxial tensile</td>
<td>[86]</td>
</tr>
<tr>
<td>Ring beams</td>
<td>Uniaxial tensile</td>
<td>[81] [85]</td>
</tr>
<tr>
<td></td>
<td>Have paper on semi-circular beams.</td>
<td></td>
</tr>
<tr>
<td>Bulge test</td>
<td>Biaxial compressive</td>
<td>[96]</td>
</tr>
</tbody>
</table>

The deflections of thin film structures can be measured using a variety of techniques including mechanical probe, atomic force microscopy (AFM), optical microscopy, laser scanning confocal microscopy (LSCM), scanning electron microscopy (SEM), laser light reflectivity and interferometric profilometry.

2.6 Uses of TiN Thin Films in MEMS

TiN has been investigated for a variety of MEMS related applications. Within these investigations, TiN was selected for its mechanical, chemical and electrical properties. De Moor and coworkers [27] investigated Ti/TiN thin films as a new material for resistive heaters. They chose Ti/TiN thin films for resistivity in the range of 50-100 μΩ.cm, which is comparable to the traditional heater material of NiCr. In addition, the fabrication of Ti/TiN heaters is CMOS compatible, whereas NiCr is not compatible with standard CMOS processing. Their investigations showed that Ti/TiN thin films are suitable as heaters in MEMS applications. Ostrick and coworkers [97] investigated TiN films in a work function type ammonia sensor. The reaction of ammonia on TiN is known to occur reversibly at room temperature and to not be hindered by preadsorption. Their work was aimed at investigating reactions for the use of TiN for gas sensing at room temperature.
TiN has been used for its optical properties in Deep UV (DUV) lithography for resist patterning [98].

The Young’s modulus and residual stress of TiN has been investigated using micromachining techniques. Karimi and coworkers [96] conducted bulge tests and nanoindentation tests on TiN films to determine Young’s Modulus and residual stress when deposited using RF magnetron sputtering. The films were deposited on n-type Si(100) wafers coated on both sides with LPCVD silicon nitride. The bulge test substrates were fabricated using standard photolithography and silicon back etching techniques. They state that compressive films are unsuitable for bulge testing due to buckling when released from the substrate. This was overcome by depositing TiN films in tension or obtain flat TiN + SiN.

Johansson and coworkers [99] magnetron sputtered submicron TiN, Al and Ti films or thermally coated with SiO$_2$ onto microscale silicon microbeams of different single crystal orientations. This was done to determine the residual stress of the films, through a derived theoretical expression that was derived from observed deflections. In addition, the maximum stress at fracture in the coatings and in the substrates was determined by applying external bending moments with the relevant theory. Figure 2.4 is an image of a SEM micrograph, taken from [100], which shows a TiN coated Si cantilevers fabricated by Johansson and coworkers [99]. The downward deflection of the cantilevers has been induced by the high compressive stress of the TiN film.

![Figure 2.4 TiN coated Si cantilevers, deflected by high compressive stress in the TiN film. From [100].](image-url)

### 2.7 Physical Properties of TiN

Table 2.3 lists properties of TiN that may be useful in the application of TiN for surface micromachining applications. The list was compiled from reliable sources, however it must be noted that most of the properties listed depend on the type of deposition used and even the deposition parameters.
Table 2.3 Physical properties of TiN

<table>
<thead>
<tr>
<th>Physical properties of TiN</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crystal structure</td>
<td>Cubic NaCl B1 [16]</td>
</tr>
<tr>
<td>Stoichiometric range</td>
<td>TiN$<em>{0.55}$ to TiN$</em>{1.05}$ [16]</td>
</tr>
<tr>
<td>Crystal structure ($\delta$-TiN$_{1-x}$)</td>
<td>FCC [101]</td>
</tr>
<tr>
<td>Unit cell length (Å)</td>
<td>4.242 [16]</td>
</tr>
<tr>
<td>Bond length (Å)</td>
<td>2.1215 [102]</td>
</tr>
<tr>
<td>Density (g/cm$^3$)</td>
<td>5.43 [60]</td>
</tr>
<tr>
<td>Elastic modulus (GPa)</td>
<td>640 [103]</td>
</tr>
<tr>
<td>Hardness (Vickers H$_V$)</td>
<td>2300 [16]</td>
</tr>
<tr>
<td>Coefficient of friction</td>
<td>~0.2 [55]</td>
</tr>
<tr>
<td>Poisson’s ratio</td>
<td>~0.3 [16]</td>
</tr>
<tr>
<td>Coefficient of thermal expansion ($^\circ$C$^{-1}$)</td>
<td>9.4 [102]</td>
</tr>
<tr>
<td>Melting temperature (°C)</td>
<td>2950 [16]</td>
</tr>
<tr>
<td>Resistivity $\rho$ (μΩ.cm)</td>
<td>90 [27]</td>
</tr>
</tbody>
</table>
Chapter 3

Experimental Methodology

This chapter covers the experimental methodology used in substrate preparation, thin film deposition, patterning used in excimer laser micromachining and wet-etching. The techniques used to characterise the thin films and the micromachining behaviour are covered.

3.1 Substrate

Single crystal silicon was selected as the substrate material. The advantage of this selection is that its mechanical properties are well characterised and Si wafers are widely available at low cost [104]. The type of silicon wafer used was (100) n-type with a thickness of 500 ± 50 μm. Wafer cleaning consisted of the standard cleaning recipe RCA1 – 10%HF – RCA2 and the following regime [105]:

1. Immerse in acetone for 1 minute, rinse in running deionised water for 3 minutes, dry with N₂.
2. RCA1 (1 H₂O₂ : 3 H₂SO₄ : 6 H₂O) for 9 minutes at 80°C, rinse in running deionised water for 3 minutes, dry with N₂.
3. 10% HF for 9 minutes at room temperature, rinse in running deionised water for 3 minutes, dry with N₂.
4. RCA2 (1 H₂O₂ : 1 HCl : 5 H₂O) for 9 minutes at 80°C, rinse in running deionised water for 3 minutes, dry with N₂.

Chapter 3 Experimental Methodology
3.2 Magnetron Sputtering

The Cr and Cu thin films were deposited using a DC balanced magnetron sputtering unit. The unit comprised of two magnetron guns, each with water-cooled copper hearths approximately 77 mm in diameter. Discs of Cr and Cu, each 77 mm in diameter and 6.7 mm thick, were used as cathodes. The pumping system comprised of a rotary vane roughing pump (40 litres/min) that was used to back a turbomolecular high vacuum pump.

Prior to deposition the chamber was evacuated to a base pressure of $4 \times 10^{-6}$ mbar. To facilitate the removal of any residual atmospheric contamination and enable good quality adhesion, the substrates were cleaned by plasma etching using $\text{Ar}^+$ for 5 minutes at $1.5 \times 10^{-2}$ mbar using a bias voltage of 900 V; the corresponding current was 25 mA. The targets were cleaned by sputtering behind shields for 10 minutes prior to the start of deposition. Sputter deposition was carried out in an Ar atmosphere at $6 \times 10^{-3}$ mbar. The current was fixed at 0.5 A (fixing the current ensured a constant deposition rate). The cathode voltage was 460 – 480 V. The distance between the cathode and substrate was fixed at 120 mm. The substrate was not heated. Upon completion of deposition the substrates were cooled in Ar at the deposition pressure for 60 minutes and then removed.

In the case of Cu deposition, a 20 nm Ti layer was deposited onto the Si to serve as an adhesion layer. This step preceded the Cu deposition in the same deposition run.

3.3 Filtered Arc Deposition

A filtered cathodic arc evaporation system was used to deposit the TiN thin films. The system comprised of twin arc evaporation sources configured in both the partial and full filtration modes. Figure 3.1 shows a schematic of the system in the partially filtered configuration.
Chapter 3 Experimental Methodology

33

Figure 3.1 Schematic of the filtered arc deposition system showing partially filtered configuration.

The partial filtration mode comprised of an axial plasma duct (200 mm diameter) fitted between the cathode source and the coating chamber. The duct was fitted with solenoid magnetic field coils that generated a magnetic field of between 90 - 140 gauss.

To increase the degree of macroparticle filtration the fully filtered configuration was utilised. Figure 3.2 shows a schematic of the system in the fully filtered configuration. In this mode the axial plasma duct was connected to a 22º knee magnetic filter duct. The knee magnetic filter duct was fitted with solenoid magnetic field coils (also 90 – 140 gauss) for guiding the trajectories of the ionised species. Apart from the difference in the modes of filtration, the rest of the system remained unchanged.
Figure 3.2 Schematic of the filtered arc deposition system showing fully filtered configuration of a 22º knee.

The cathode source (diameter; 58 mm: length ~35 mm) was mounted on water-cooled Cu hearths. Internal Cu anodes (diameter; 190 mm: length 200 mm) were used; each was water-cooled and electrically isolated from the plasma duct. A pneumatic trigger of tungsten wire, activated by an automatic control system, was used to initiate the arc. The chamber was evacuated to a base pressure of $1.3 \times 10^{-4}$ mbar. The substrates were subjected to a 10 minute N$^+$ etch at room temperature using a hot anode – cold cathode source with a discharge voltage of 2.0 kV and a discharge current of 150 mA [31], [106]. The TiN was deposited at an arc current of 100 A, a bias voltage of $-150$ V and a nitrogen pressure of $6-7 \times 10^{-3}$ mbar. Substrates were either preheated to approximately 200ºC or not preheated at all. Radiant heaters were used to heat the substrates. The temperature inside the chamber was monitored using a thermocouple. When depositing in the partially filtered mode the substrates were rotated at 8 RPM using planetary rotation. In the case of fully filtered deposition, the substrates were held stationary in front of the filter duct.
3.4 Excimer Laser Micromachining

Laser micromachining was carried out using an excimer laser system (Series 8000 (Exitech Limited, UK) equipped with a Lambda Physik LPX210I laser source). Figure 3.3 shows a block diagram of the system.

Figure 3.3 Block diagram showing the excimer laser system.

The system delivered the laser energy to the workpiece via an attenuator, beam shaping and homogenisation optics and a lens arrangement. The attenuator consisted of a dielectrically coated plate and an uncoated compensator plate angularly rotated in the beam to continuously change the optical transmission value [107], [108], [109]. A double fly’s eye homogeniser having a numerical aperture (NA) of 0.01 produced a 12 mm × 12 mm (or 9.5 mm × 9.5 mm) uniform, square beam at the plane of a chrome-on-quartz mask plane. The mask was held on an open frame with a computer numerically controlled (CNC) stage. The lens used for this work had a 1:10 demagnification factor, NA of 0.3, a 1.5 mm diameter field and an optical resolution of 0.8 μm. The arrangement of the homogeniser and the lens produced a partial coherence factor of 0.2. An on-line beam profiler monitored the pulse energy, of which, 80% had an intensity variation of less than ± 5% RMS. The laser had a pulsewidth of 20 ns, which enabled material to be ablated with a depth resolution in the order of 0.1 μm. The spatial resolution was around 1 μm or better. The maximum pulse repetition rate was 100 Hz.
Laser patterning was performed using KrF radiation at $\lambda = 248$ nm. The laser fluence ranged from 0.58 to 7.4 J/cm$^2$. The value of 7.4 J/cm$^2$ was achieved by removing the attenuator. Machining was carried out using 1, 2, 4, 8, 16, 32 and 64 pulses. A repetition rate of 3 Hz was used (single pulse conditions). Laser pulse energies were calibrated at the workpiece using a pyroelectric energy monitor (Molelectron Type JD25). A test pattern with pitches ranging from 2 to 40 $\mu$m was used to determine the patterning quality and the ability to selectivity remove TiN with minimal interference to the underlying metal sacrificial layers. The laser micromachining process is represented by the schematic shown in Figure 3.4.

![Figure 3.4 Laser micromachining steps used to pattern TiN from Cr and Cu layers showing (a) excimer laser irradiation, (b) the patterned TiN thin film on a sacrificial layer.](image)

### 3.5 UV Photolithography and Wet-etching

UV photolithography and wet-etching were also used to pattern TiN. The process strategy used is represented by the schematic shown in Figure 3.5. The strategy consisted of a Cr sacrificial layer sputtered onto Si, followed by deposition of a TiN layer and then sputtering of a Cr etch mask (contact mask) over the TiN. The use of a Cr etch mask was employed as preliminary attempts to etch the TiN with only a photoresist
AZ1512 were unsuccessful as the photoresist was readily attacked by the TiN etchant, SC-1.

![Figure 3.5 Fabrication steps used to wet-etch TiN showing (a) exposure of photoresist with mask aligner radiation, (b) etching of the Cr contact mask, (c) etching TiN thin film on sacrificial layer, (d) contact mask removal and sacrificial etch of Cr to release TiN structure.](image)

The Cr contact mask was sputtered onto the TiN layer to a thickness of approximately 200 nm. Photoresist AZ1512 was spin-coated over the Cr to a thickness less than 2 μm and baked in air at 90°C for 20 minutes. The photoresist was exposed using a UV mask aligner at a wavelength of 425 nm. The photoresist was developed in AZ400K developer for 30 seconds. The Cr contact mask was etched using CEP-200 micro-chrome etchant. The photoresist was stripped using acetone. The acetone residue was removed by soaking the sample in ethanol and rinsing in deionised water. The TiN was etched in SC-1, which contained deionised water, 30 wt% H₂O₂ and 30 wt% NH₄OH in the ratio 5:1:1. After the TiN etch step was completed the Cr contact mask was wet-etched using the CEP-200 micro-chrome etchant. This step also saw the etching of the Cr sacrificial layer and the undercutting of the TiN thin film. All wet-etching was conducted at room temperature without stirring.
3.6 Scanning Electron Microscopy (SEM)

SEM analysis was used to provide topographical representation of a specimen and where appropriate composition of the near surface regions of the specimen. Information was obtained through secondary electron images, backscattered electron images and X-ray analysis (EDS). SEM analysis was carried out using two scanning electron microscopes. The more utilised of the two scanning electron microscopes was a Philips XL-30 SEM, which was operated at accelerating voltages in the range of 10-30 kV. The XL-30 SEM employed a LaB$_6$ filament as the electron source and was fitted with a suite of detectors including a secondary electron detector, backscattered electron detector and an X-ray detector. The less utilised of the two scanning electron microscopes was a JEOL JSM840 SEM, which was operated at accelerating voltages in the range of 15 kV. The JEOL JSM840 SEM was equipped with a backscatter electron detector and a Tracor Northern X-ray detector for EDS analysis.

EDS analyses were carried out at an acceleration voltage of 10 kV. An acceleration voltage of 10 kV equates to an incident beam energy of 10 keV. An incident beam energy of 10 keV was selected for two reasons; (1) 10 keV corresponds to a beam/material interaction volume of around 1 $\mu$m$^3$, which makes EDS suitable for analysing the composition of micropatterned features with dimensions as small as 5 $\mu$m without obtaining misrepresentative information from non-patterned regions due to beam spread; (2) the elements Si, Ti, Cr and Cu were of interest and an incident beam energy of 10 keV provided for the detection of these elements as the X-ray energies of their respective $K$ and $L$ electron shells are below 10 keV [110], as shown in Table 3.1.

<table>
<thead>
<tr>
<th>Element</th>
<th>Atomic number</th>
<th>$K_{\alpha}$</th>
<th>$K_{\beta}$</th>
<th>$L$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si</td>
<td>14</td>
<td>1.739</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ti</td>
<td>22</td>
<td>4.508</td>
<td>4.931</td>
<td>0.452</td>
</tr>
<tr>
<td>Cr</td>
<td>24</td>
<td>5.411</td>
<td>5.946</td>
<td>0.573</td>
</tr>
<tr>
<td>Cu</td>
<td>29</td>
<td>8.040</td>
<td>8.804</td>
<td>0.930</td>
</tr>
</tbody>
</table>

Table 3.1 Energies (in keV) of characteristic X-rays of the elements Si, Ti, Cr and Cu. From [110].
3.7 Laser Scanning Confocal Microscopy (LSCM)

LSCM was used to provide topographical representation in the form of images and surface roughness of samples. LSCM was carried out on both the Olympus OLS1100 and OLS1200 models. The microscope was used to generate three-dimensional images through the use of a He:Ne laser and a stage that could step 10 nm in the z-direction.

3.8 Rutherford Backscattering Spectroscopy (RBS)

RBS is a non-destructive technique that can detect light and heavy elements and has proved to be a powerful tool for use in the semiconductor industry for the analysis of thin films and determining the composition of doped polysilicon. RBS is now a commonly used analysis technique for determining elemental composition and depth profiling.

RBS uses a mono-energetic and collimated beam of alpha particles (\(^{4}\text{He}^+\) nuclei) of known energy incident on a target. Some alpha particles undergo elastic collision with target atoms and are backscattered away from the target surface with a reduced energy. A detector determines the energy distribution and yield of the backscattered particles, which leads to identification of the target nuclei and its concentration in the target material. The ratio of the scattered beam energy \(E'\) to the incident beam energy \(E\) is the kinematic factor, \(K\). The kinematic factor is expressed as:

\[
K = \frac{E'}{E} = \left( \frac{m_1 \cos \theta + \sqrt{m_2^2 - m_1^2 \sin^2 \theta}}{m_1 + m_2} \right)^2 = \left( \frac{1 - \left( \frac{m_1}{m_2} \right)^2 \sin^2 \theta + \left( \frac{m_1}{m_2} \right) \cos \theta}{1 + \left( \frac{m_1}{m_2} \right)^2} \right)^2 
\]

where \(m_1\) and \(m_2\) are the masses in atomic mass units (amu) of the alpha particle and the target atom respectively and \(\theta\) is the scattering angle [111]. The kinematic factor depends only on the ratio of the masses of the alpha particles and the target nuclei and the scattering angle \(\theta\). Figure 3.6 shows a schematic of the backscattering events that occur at the surface of the target and at a depth \(\delta t\).
Figure 3.6 Schematic of beam-specimen interaction of RBS analysis. From [111].

The energy of the backscattered yield is attenuated by the target matrix, and therefore is uniquely determined by the depth and scattering element(s) present. When analysing thin films the energy loss is considered to vary linearly with thickness and as a result provides a depth profile.

The yield is determined by the differential scattering cross section, $\frac{d\sigma}{d\omega}$:

$$\frac{d\sigma}{d\omega} = \left(\frac{Z_1 Z_2 e^2}{4E}\right)^2 \cdot \left(\frac{\cos \theta \sqrt{1 - \left(\frac{m_1 \sin^2 \theta / m_2\right)^2}}}{\sin^4 \theta \sqrt{1 - \left(\frac{m_1 \sin^2 \theta / m_2\right)^2}}\right)^2$$  \hspace{1cm} (12)

where $Z_1$ and $Z_2$ are the ion beam atomic number and the target atomic number respectively, $E$ is the incident ion beam energy (MeV), $e$ is the charge constant and $\theta$ is the scattering angle. The differential scattering cross section is basically proportional to the square of the atomic number of the target atoms, which means that RBS is more sensitive for heavier atoms [65].

The main disadvantage of RBS analysis is that the output of detected species can overlap. Overlapping creates difficulties in determining the thickness of a film when the detected element(s) are significantly lighter or close in atomic mass to that of the substrate. Hence, the best results are achieved when analysing heavy elements on light substrates.

RBS was performed using a 2.0 MeV $^4$He$^+$ ion beam accelerated by a Van de Graaff accelerator. The particle beams were focused and collimated to a diameter of approximately 1 mm. The detector was fixed at 169º to the beam direction. Spectra were accumulated for an incident charge of $Q = 20 \mu$C which equates to $1.25 \times 10^{14}$ ions. This was measured using a sensitive Faraday cup arrangement. The detector was connected to a multi-channel analyser, which counted the beam scattered yield from the sample. Prior to analysis a system calibration was carried out using samples of C, Al, Si, Ti and Cu in order to provide a means for determining the channel width ($\varepsilon$) and the offset of the multi-channel analyser.
RBS spectra were analysed for stoichiometry, composition and thickness using the software package RUMP. RUMP is an essential tool for the analysis of RBS spectra as it enables interpretation by closely matching experimental spectra with simulated spectra. Difficulties arise in accurately simulating an experimental spectrum where elements are close in atomic number and also in cases where composition gradients are present [112].

RBS was used to determine the composition and depth profile of films in the deposited state and after laser micromachining and wet-etching. The analysis of micromachined sub-millimetre features using RBS was not possible due to the diameter of the incident beam being around 1 mm. Hence, in order to analyse laser patterned sites, samples were prepared with sufficient area to compensate for the diameter of the beam. Samples were laser patterned using a 600 \( \mu \text{m} \times 600 \mu \text{m} \) feature in an array of \( 6 \times 6 \) to provide a total irradiated area of approximately 13 mm\(^2\). Figure 3.7 shows a schematic, with relative dimensions, of the 13 mm\(^2\) laser patterned area and the nominal location of the 1 mm diameter incident beam during analysis. It can be seen from the schematic that the incident beam had sufficient area to only analyse the laser patterned region and not impinge on the surrounding non-machined region.
3.9 X-Ray Diffraction (XRD)

XRD is a technique used to investigate the crystal structure of materials including crystal orientation, strain state, grain size, epitaxy and defect structure. Central to the interpretation of XRD is Bragg’s Law, which governs the diffraction of X-rays from crystal planes parallel to the surface of the sample. Crystal structures are long range ordered, three-dimensional arrays of atoms in space and based on a basic repeating pattern. A consequence of this is that a crystal consists of planes of atoms. A crystal consists of a variety of crystal planes or atomic planes, all of which have a distinct interplanar spacing or d-spacing. The planes of a crystal are described using planar indices or Miller’s indices or simply as h,k,l in parenthesis, (hkl), with the d-spacing of a given plane denoted as $d_{hkl}$ [113]. Bragg’s Law is satisfied when an incident beam of X-rays is reflected because of constructive interference, hence;

$$n\lambda = 2.d_{hkl} \sin \theta_{hkl}$$

(13)

where $\theta_{hkl}$ is called the Bragg angle and is measured between the incident beam and the particular crystal planes being considered and $\lambda$ is the wavelength of the incident X-rays [114]. The diffracted X-rays are detected at an angle of $2\theta$, typically called the diffraction angle. Figure 3.8 shows a schematic of diffraction of X-rays from a set of crystal planes.
Bragg Brentano XRD was used in this work to determine crystal orientation including preferred orientation and the strain state of TiN thin films. XRD analysis was carried out using a Siemens D500 glancing angle X-ray diffractometer. The spectra were obtained using Co Kα X-ray radiation in the 2θ ranges; 35 to 75° with a step size of 0.05°.

3.10 Secondary Ion Mass Spectrometry (SIMS)

SIMS is an ion beam analysis technique used to characterise materials up to a depth of 10 μm. SIMS is a destructive technique that detects the energy of secondary ions that are sputtered from a surface by high-energy incident ions. Sputtering can be carried out by Cs+, O2+, O, Ar+ or Ga+ ions at energies between 2 and 50 keV. The incidence of the primary ion beam causes a collision cascade that ejects secondary particles that are monoatomic, polyatomic, molecules or clusters of atoms. Fractions of the secondary particles are secondary ions. The secondary ions are separated using an ion optics arrangement and detected using a faraday cup or electron multiplier. Only specific ions are selected for detection and this is based on their trajectory and kinematic energy range. SIMS information can be presented in three ways:

- Mass (amu). The top monolayer is analysed in a technique known as static SIMS (SSIMS).
- Depth profile of selected elements. The top monolayer is continuously sputtered as a function of time (Dynamic SIMS).
- Surface composition mapping. The top monolayer is analysed and presented as a function of position on the surface.
Depth profiling is commonly used to characterise semiconductor materials and thin films. In depth profiling, a crater is formed by continuously sputtering to create fresh surface. Typically, a raster pattern is used to ensure uniformity of the crater and that only the laterally distributed elements are detected. When performing depth analysis, the user must be aware that the analysis of uneven craters, arising from uneven surfaces, can result in depth variations that lead to misrepresentation of the depth profile [115].

SIMS has a depth resolution of 2-10 nm, which makes it a very attractive technique for investigating surface impurities and interface thickness. SIMS is also highly sensitive with detection limits of \(10^{13} - 10^{18}\) atoms/cm\(^3\) for semiconductors [111]. In the case of depth profiling using SIMS, each nominated element has its own spectral line. This has the advantage of eliminating spectral overlap, which is a problem that can inhibit the interpretation of RBS spectra. However, unlike RBS, SIMS spectra require adjustment from a time scale to a depth scale. This can be achieved by either measuring the crater depth using a profilometer or a laser scanning confocal microscope, or alternatively by the following relationship in which the depth, \(z\), is related to the product of the ion beam current density \(J\) (A/cm\(^2\)), the sputtering time \(t\) (s) and the sputter yield \(Y\) (atoms/ion) of the sample:

\[
z = \frac{YJMt}{1000e\rho N_A n}
\]  

(14)

where \(e\) is the electric charge, \(M\) is the target molecular weight, \(\rho\) is the target atomic density (kg/m\(^3\)), \(N_A\) is Avogadro’s number and \(n\) is the number of atoms in the molecule. These methods are accurate for low concentration atoms (<10%) in a uniform matrix, but become unreliable when investigating multilayers due to variation in the sputter yield \(Y\) with composition. In this work, laser scanning confocal microscopy was used to measure crater depths to facilitate the adjustment of the time scale to a depth scale.

The main disadvantage of SIMS is the difficulty in relating the strength of the SIMS signal to the composition of the surface. This is because a theory allowing absolute or relative quantification has not yet been provided. Typically, this is overcome by comparing obtained spectra with characterised standards [111]. The SIMS was carried out using a Cameca ims 5f system equipped with a duoplasmatron source and
employing a Cs\(^+\) ion-sputtering source. The detectors were an electron multiplier to faraday cup, which occurs at a count rate of \(\sim 10^6\) counts/sec. The crater dimensions were typically 100 \(\mu\)m \(\times\) 150 \(\mu\)m.
Chapter 4

Laser Patterning of Partially Filtered TiN Thin Films

This chapter presents the excimer laser micromachining of partially filtered TiN thin film. The patterning process should selectively remove the TiN thin film from the underlying material (substrate or sacrificial layer) with a high degree of patterning quality and feature replication and with minimal impact to underlying materials. The following parameters that were thought to influence the patterning quality of TiN were investigated: different sacrificial materials; laser fluence; number of pulses; feature size and TiN deposition temperature. The quality of the laser patterning was carried out by evaluating edge quality, quality of pattern replication, degree of TiN removal and amount of damage induced to the underlying material. Analytical techniques that determine composition were used to characterise laser patterned sites and evaluate the occurrence of selective TiN removal.

4.1 Characterisation of Partially Filtered TiN

The stoichiometry of TiN was analysed using RBS analysis and RUMP simulations. Figure 4.1 shows experimental and simulated spectra of a 554 nm thick TiN thin film deposited at room temperature onto a Si substrate. In illustrative terms, two distinct aspects of the spectrum confirm the detection of a TiN thin film on top of Si. One, the leading edge of the spectrum at channel 363 corresponds to the backscattered energy of Ti and two, the rise in the number of counts at channel 155 corresponds to the backscattered energy of N. The presence of a 554 nm TiN thin film on top the Si has caused attenuation in the energy of the Si backscattered yield and is shown by the rise in
number of counts at channel 136. Simulation of the spectrum indicated that the TiN was stoichiometric with a Ti:N ratio of 1:1. Separate RUMP simulations (not shown) employing a Ti:N ratio of 1:0.95 and 1:1.05 were carried out and achieved a poorer match to the experimental spectra. Hence, interpretation of simulated spectra reveals the stoichiometry to be TiN$_{1.0}$ with an uncertainty of ± 2.5%. Additionally, it can be seen that the RBS signal is not zero between channels 160 and 200. This is because pinhole defects in the TiN thin film enabled the detection of Si (resulting in a Si contribution) without the expected attenuation in the backscattered yield arising from the presence of the 554 nm thick TiN thin film.

![Figure 4.1 RBS spectra (experimental and simulated) showing a 554 nm thick TiN$_{1.0}$ film on Si.](image)

Figure 4.1 RBS spectra (experimental and simulated) showing a 554 nm thick TiN$_{1.0}$ film on Si.

Figure 4.2 shows a SEM micrograph of a cross-section of a ~9 μm thick TiN thin film deposited onto (100) Si. The cross-section was obtained by fracturing the sample. The image clearly shows the columnar structure of the TiN through the presence of parallel rod-shaped columns, which are up to 200 nm across. The deposition of such a thick film was carried out to show the columnar structure of cathodic arc deposited TiN and was achieved by holding the substrate stationary in the deposition stream.
Figure 4.2 SEM micrograph of a cross-section of a ~9 μm thick partially filtered TiN thin film on Si showing the columnar structure of the TiN through the presence of parallel rod-shaped grains.

XRD was carried out to determine the preferred orientation of partially filtered TiN deposited on Si and on a Cr sacrificial layer. As a precursor, XRD was carried out on Si (100) substrate, with the indexed spectrum shown in Figure 4.3. The peak at 2θ = 38.5° corresponds to Si (200). The peak situated at 2θ = 73.2° corresponds to Si (400).

Figure 4.3 XRD spectrum of Si (100) substrate showing the Si (200) and Si (400) peaks at 2θ = 38.5° and 73.2°.

Figure 4.4 shows an indexed XRD spectrum of partially filtered TiN deposited at room temperature onto Si. The TiN has contributed three peaks; (111) at 2θ = 42°, (200) at 2θ = 50° and (220) at 2θ = 73.3°. The peak located at 2θ = 73.3° is a likely to be a
combination of the TiN (220) and the Si (400) peaks. The TiN shows a strong (111) preferred orientation, which is consistent with previous observations [32], [116], [117].

Figure 4.4 XRD spectrum of partially filtered TiN deposited at room temperature on Si showing three possible TiN peaks; (111) at $2\theta = 42^\circ$, (200) at $2\theta = 50^\circ$ and (220) at $2\theta = 73.3^\circ$. The preferred orientation of the TiN is (111).

Figure 4.5 shows the indexed XRD spectrum of partially filtered TiN deposited onto Cr sacrificial layer at room temperature. The TiN shows a (111) preferred orientation. The peak observed at $2\theta = 52.3^\circ$ was indexed to that of Cr (110). Separate XRD analysis of Cr on Si (not shown) indicated the respective Si and Cr peaks.
Figure 4.5 XRD spectrum of partially filtered TiN deposited at room temperature onto Cr on Si showing a TiN (111) preferred orientation.

TiN thin films were also deposited onto Cr at 200°C. Figure 4.6 shows the indexed spectra of partially filtered TiN deposited onto Cr at room temperature and 200°C. Both spectra show that the TiN has a (111) preferred orientation. It should be noted that the (111) peak of TiN deposited at room temperature has shifted to a lower 2θ value relative to that of the TiN thin film deposited at 200°C. The reason for the peak shift of the TiN deposited at room temperature to a lower 2θ value is due to the relative increase in compressive stress of the TiN. Superficially, an increase in compressive stress causes a decrease in the diffraction angle, since crystal planes parallel to the surface compress elastically causing a corresponding increase in the d-spacing of the crystal. A more thorough description of the relationship between compressive stress and the diffraction angle is contained in section 7.3.
One of the central themes of this investigation was the need to selectively remove the thin film materials from one another. Selectively removing one material from another means that complete separation at the interface must occur. Hence, obtaining information about an interface is important in determining the removal behaviour of one material from another. SIMS analysis was carried out to determine the thickness of the TiN/Cr interfaces of partially filtered TiN deposited onto Cr at room temperature and 200°C. The thickness of the TiN/Cr interfaces provides an indication of the quality of contact between the TiN and Cr. A thick interface is indicative of poorer contact, possibly due to the presence of voids at the interface causing an uneven crater and introducing depth variation. Conversely, a narrow interface indicates a high degree of contact between the TiN and Cr layers. It should be noted that TiN/Cr interface thickness values as determined by SIMS analysis have only been provided for comparison purposes and are not intended to serve as absolute values.

Figure 4.7 shows SIMS spectra for partially filtered TiN deposited at room temperature. The thickness of the TiN/Cr interface was determined by subtracting the depth at which the Cr spectrum starts to rise (~270 nm) from the depth that corresponds to the y-axis value of the Ti spectrum (~417 nm). In this case, the thickness of the TiN/Cr interface was estimated to be around 147 nm thick.
Figure 4.7 SIMS spectra of partially filtered TiN deposited onto Cr at room temperature showing TiN/Cr interface to be around 147 nm thick.

Figure 4.8 shows the SIMS spectra for partially filtered TiN deposited at 200ºC. Using the same method the thickness of the TiN/Cr interface was approximately 100 nm thick.

Figure 4.8 SIMS spectra of partially filtered TiN deposited onto Cr at 200ºC showing TiN/Cr interface to be around 100 nm thick.
4.2 Selective Removal of TiN Thin Film

Using Si as an underlying material, partially filtered TiN was deposited at room temperature to a thickness of ~554 nm. Figure 4.9(a) shows a confocal micrograph of the TiN thin film laser patterned at a fluence of 1.60 J/cm² using eight pulses. Laser patterning was carried out using a 15 μm feature. Dashed lines superimposed over images have been added to highlight the irradiated regions in this image and subsequent images. The quality of laser patterning of the TiN thin film is extremely poor and to assist in distinguishing the irradiated regions from the non-irradiated regions the abbreviation I-R (Irradiated-Region) has been superimposed over the image. Figure 4.9(b) shows an EDS spectrum obtained from inside the patterned region, which indicates through the presence of the Si $K\alpha$ peak and the absence of any significant Ti peaks that the TiN thin film was completely removed. It must be noted that a small Ti peak is present at 4.5 keV and that is was most probably due to the detection of recoiled TiN debris on the surface of the Si.

![Figure 4.9](image)

Figure 4.9 (a) Confocal micrograph of a ~554 nm thick partially filtered TiN thin film on Si laser patterned at a fluence of 1.60 J/cm² using eight pulses (b) EDS spectrum obtained from the patterned region.

Using Cu as a sacrificial layer, partially filtered TiN thin film was deposited at room temperature to a thickness of ~400 nm onto a ~700 nm thick Cu film on Si. Figure 4.10(a) shows a confocal micrograph of the TiN thin film laser patterned at a fluence of 1.50 J/cm² using one pulse. Laser patterning was carried out using a 20 μm feature.
EDS analysis was carried out inside the patterned region, with the spectrum shown in Figure 4.10(b). The presence of only the Cu \( K\alpha \), Cu \( K\beta \), and Cu \( L \) peaks signify the exposure of the Cu sacrificial layer and indicate the removal of the TiN thin film.

![EDS spectrum](image)

Figure 4.10 (a) Confocal micrograph of ~400 nm thick partially filtered TiN thin film on a ~700 nm thick Cu sacrificial layer on Si laser patterned using a 20 \( \mu \text{m} \) feature at a fluence of 1.50 J/cm\(^2\) using one pulse (b) EDS spectrum indicating exposure of the Cu sacrificial layer.

Using Cr as a sacrificial layer, partially filtered TiN was deposited at room temperature to a thickness of ~420 nm onto a Cr film ~1000 nm thick. Figure 4.11(a) shows a SEM micrograph of the TiN laser patterned at a fluence of 1.60 J/cm\(^2\) using one pulse. Laser patterning was carried out using a 20 \( \mu \text{m} \) feature. EDS analysis was carried out inside the patterned region, with the spectrum shown Figure 4.11(b). The presence of only the Cr \( K\alpha \), Cr \( K\beta \) and Cr \( L \) peaks signify the exposure of the Cr sacrificial layer and indicate the selective removal of the TiN thin film.
Figure 4.11 (a) SEM micrograph of ~420 nm thick partially filtered TiN thin film on a ~1000 nm thick Cr sacrificial layer on Si laser patterned using a 20 μm feature at a fluence of 1.60 J/cm$^2$ using one pulse (b) EDS spectrum showing only Cr peaks indicating the selective removal of the TiN thin film.

The results show that TiN can be selectively removed using an excimer laser from Si (100) substrate, Cu sacrificial layer and Cr sacrificial layer, however the quality of patterning varied for each underlying material. The next section covers a further investigation of this aspect of the work.

4.3 Laser Patterning of TiN from Underlying Materials

4.3.1 Si (100) Substrate

TiN was deposited on Si (100) substrate at room temperature to a thickness of ~554 nm. The TiN was laser patterned at a fluence of 1.60 J/cm$^2$. Laser patterning using one pulse did not remove the TiN thin film, however fine cracks were observed over the surface of the irradiated region. Laser patterning with four pulses caused an increase in the number and severity of the cracks. Figure 4.12(a and b) show confocal micrographs of TiN thin film laser patterned using 32 and 64 pulses respectively. Laser patterning was carried out using a 15 μm feature. Laser patterning the TiN thin film with 32 pulses resulted in extremely poor quality patterning. Increasing the number of pulses to 64 resulted in an increase of TiN removal, however there was no improvement in the quality of patterning in terms of both feature replication and edge definition. In terms of the
quality of patterning and feature replication, the laser patterning of TiN from Si proved inconsistent and unsatisfactory.

Figure 4.12 Confocal micrographs of a ~554 nm thick TiN thin film on Si (100) substrate laser patterned with a 15 μm feature at a fluence of 1.60 J/cm² using (a) 32 and (b) 64 pulses.

4.3.2 Cu Sacrificial Layer
TiN thin films were deposited at room temperature to a thickness of ~400 nm onto Cu sacrificial layers. Laser patterning was carried out at a fluence of 1.50 J/cm² using a 20 μm feature. Figure 4.13(a-c) show confocal micrographs of TiN thin film on a ~700 nm thick Cu sacrificial layer patterned using one, two and four pulses respectively. Laser patterning with one pulse resulted in poor quality patterning as is evident from the poor edge quality. Furthermore, the exposed Cu surface shows a considerable amount of damage in the form of surface craters. Further exposure to two and four pulses was carried out to determine if improvements to the quality of patterning could be obtained. The extra pulses did not improve the quality of patterning, however the surface of the Cu does appear to have less craters. Smoothing of the Cu surface of this nature is most probably a result of incipient melting.
Chapter 4 Laser Patterning of Partially Filtered TiN Thin Films

To understand the effect of sacrificial layer thickness, laser patterning was also carried out on a sample having a ~400 nm thick Cu layer and ~400 nm thick TiN layer. In this case the Cu sacrificial layer was damaged and peeled from the Si substrate. In terms of the quality of patterning and feature replication, the laser patterning of TiN from Cu sacrificial layer proved to be unsatisfactory.

4.3.3 Cr Sacrificial Layer

TiN thin films were deposited to a thickness of ~420 nm at room temperature onto a Cr sacrificial layer (thickness ~1000 nm). Laser patterning was carried out at a fluence of 1.60 J/cm² using a 20 µm feature. Figure 4.14(a-c) show SEM micrographs of TiN patterned using one, two and four pulses respectively. Laser patterning with one pulse showed high quality patterning of the TiN thin film, which is highlighted by the sharp contrast between the patterned area and the remaining TiN. Exposure to a second pulse resulted in melting of the exposed Cr. The surface morphology of the Cr is almost identical to that observed by Lee and Na [69] in their investigation of KrF excimer laser micromachining of 100 nm thick Cr film on a glass substrate. They described the morphology as “irregular long islands not connected to each other”. Melting of the Cr surface to this extent is undesirable. Laser patterning with four pulses did not improve the quality of patterning of the TiN, however, the exposed
Cr surface has a smoother morphology than after exposure to two pulses; a phenomenon that is attributed to melt flow.

Figure 4.14 SEM micrographs of ~420 nm thick TiN thin film on a ~1000 nm thick Cr sacrificial layer on Si laser patterned using a 20 μm feature at a fluence of 1.60 J/cm$^2$ using (a) one (b) two and (c) four pulses.

Figure 4.15(a) shows a SEM micrograph of a laser patterned TiN cantilever. The TiN thin film was ~420 nm thick on Cr and was laser patterned at a fluence of 1.22 J/cm$^2$. The image in Figure 4.15(b) is a higher magnification SEM micrograph of the section highlighted by the white rectangle in Figure 4.15(a), and shows that the edge quality of the patterned feature is extremely high.
Figure 4.15 SEM micrographs of a TiN cantilever laser patterned at a fluence of 1.22 J/cm$^2$ into a ~420 nm thick TiN thin film on Cr showing (a) the entire cantilever and (b) a section of the edge showing extremely high quality patterning.

The quality of TiN patterning from Cr was superior to both Cu and Si. Therefore, all subsequent laser patterning experiments were carried out using Cr as the sacrificial layer.

**4.4 Laser Patterning of TiN on Cr Sacrificial Layer**

4.4.1 Selective Removal of TiN Thin Film

RBS was used to characterise the selective removal of TiN from Cr. The TiN thin film was deposited at room temperature to a thickness of ~425 nm onto a Cr sacrificial layer (thickness ~1000 nm). Laser patterning was carried out at a fluence of 1.22 J/cm$^2$ with one pulse per area. Figure 4.16 shows a SEM micrograph of part of the patterned site prepared for RBS.
Figure 4.16 SEM micrograph of a RBS sample of ~425 nm thick TiN thin film on ~1000 nm thick Cr sacrificial layer showing laser patterning at a fluence of 1.22 J/cm$^2$ using one pulse.

Figure 4.17 shows the RBS spectrum obtained from the laser patterned region. The spectrum is typical of a Cr film as the leading edge of the spectrum corresponds to the backscattered energy of Cr. Simulation of the spectrum revealed a ~1000 nm thick Cr film containing 17% O. The absence of a Ti yield confirms that the TiN thin film was selectively removed from the Cr sacrificial layer.

Figure 4.17 RBS spectra (experimental and simulated) showing the presence of a Cr film with 17% O. Laser patterning was carried out at a fluence of 1.22 J/cm$^2$ using one pulse per area.
Chapter 4 Laser Patterning of Partially Filtered TiN Thin Films

The impact of laser patterning TiN thin film on a Cr sacrificial layer using a single pulse was determined using high magnification scanning electron microscopy. Figure 4.18 shows a SEM micrograph of a partially filtered TiN thin film laser patterned at a fluence of 1.60 J/cm$^2$. The image shows that the laser patterning process has induced cracks in the Cr film, with one of the observed cracks highlighted by the white arrow. This level of cracking is minimal and would not jeopardise the integrity of subsequent planar fabrication steps.

![SEM micrograph of a partially filtered TiN thin film on Cr on Si laser patterned using a 20 μm feature at a fluence of 1.60 J/cm$^2$ using one pulse showing a crack in the Cr film induced by the laser patterning process.](image)

4.4.2 Role of Laser Fluence

Figure 4.19(a and b) are SEM micrographs and (c) a confocal micrograph of the same sample laser patterned using one pulse at fluences of 1.60, 1.22 and 0.99 J/cm$^2$ respectively. Figure 4.19(a) has already been described and serves only as a reference. Figure 4.19(b) shows that patterning at a reduced fluence of 1.22 J/cm$^2$ resulted in poorer quality patterning of the TiN thin film. Furthermore, it can be seen in Figure 4.19(c) that reducing the fluence to 0.99 J/cm$^2$ resulted in the TiN thin film not being selectively removed at all (it must be noted that this image is a light intensity image and has been included to highlight the patterned area, even though selective patterning did not occur).
Chapter 4 Laser Patterning of Partially Filtered TiN Thin Films

Figure 4.19 Micrographs of TiN on Cr on Si, laser patterned using a single pulse at fluences of (a) 1.60 J/cm$^2$ (SEM micrograph) (b) 1.22 J/cm$^2$ (SEM micrograph) and (c) 0.99 J/cm$^2$ (confocal micrograph).

RBS was carried out on two different partially filtered TiN on Cr on Si samples with both having comparable TiN thin film thickness of ~420 nm ± 20 nm. Figure 4.20(a and b) show RBS spectra obtained from TiN thin films on Cr laser patterned using one pulse per area at fluences of 1.22 and 0.99 J/cm$^2$ respectively. The spectrum of Figure 4.20(a) has been previously shown and described as Figure 4.17 (section 4.4.1) and is shown again for comparison purposes only. To reiterate, at a fluence of 1.22 J/cm$^2$ the TiN thin film was selectively removed from the Cr film and at a fluence of 0.99 J/cm$^2$ the TiN thin film was not removed from the Cr film. The spectrum in Figure 4.20(b) shows that the leading edge (channel 372) corresponds to the backscattered energy of Ti, indicating that a TiN thin film was present on the surface of the sample after laser patterning. The higher counts around channel 264, producing the peak, represent the overlap of the Ti and Cr yields. The Cr edge has shifted to a lower energy from channel 381 to channel 263 due to attenuation of the Cr backscattered yield caused by the presence of the
unablated TiN thin film on top of the Cr. It must be noted that the analysis of TiN thin films on Cr using RBS analysis can be difficult because the elements Ti and Cr are close in atomic number (Ti-22, Cr-24) and therefore the combined yields representing the thicknesses of each element is prone to overlapping. Consequently, the greatest difficulty arises when the TiN thin film is only a few tens of nanometers thick or less. Because the unablated TiN thin film was hundreds of nanometers thick the overlapping in the Ti and Cr yields posed no problems in determining the presence of the ablated TiN thin film.

These results show that a ~420 nm ± 20 nm thick partially filtered TiN thin film deposited at a room temperature requires a minimum laser fluence of 1.22 J/cm² to be selectively removed from Cr.

4.4.3 Effect of Feature Size

The quality of laser patterning is important when fabricating a structure to design and having insight into the limitation of the patterning technique used will enable fabrication strategies to be designed according to such limitations. This means understanding the role of feature on the actual film patterning and the minimum feature size that can be
patterned. The feature sizes investigated are test features with linewidths that range from 15 μm to 2.5 μm. The set of SEM micrographs of Figure 4.21(a-e) show the result of laser patterning at a fluence of 1.22 J/cm² using 15, 10, 7.5, 5 and 2.5 μm test features respectively. Selective removal of the TiN thin film from Cr was observed for all feature sizes except the smallest at 2.5 μm. The 15 μm feature shows the best edge quality and pattern replication. Compared to the 15 μm feature, patterning of the 10 μm feature resulted in poorer edge quality and poorer pattern replication as the ends became rounded and jagged. The 7.5 μm and 5 μm features exhibit a further reduction in both edge quality and pattern replication. Hence, a trend of reduced patterning quality with feature size is evident. Overall, these results show that the laser patterned TiN thin film exhibited both reasonable edge quality and pattern replication for features down to 5 μm.
Figure 4.21 SEM micrographs of TiN on Cr laser patterned using a single pulse with test features of (a) 15 μm irradiated at 1.22 J/cm², (b) 10 μm irradiated at 1.22 J/cm², (c) 7.5 μm irradiated at 1.22 J/cm², (d) 5 μm irradiated at 1.22 J/cm², (e) 2.5 μm irradiated at 1.22 J/cm².

4.4.4 Multiple Pulse Patterning

Multiple pulse patterning was carried out to determine the impact of laser patterning on the Cr sacrificial layer after the TiN thin film was removed. Figure 4.22(a-c) shows SEM micrographs of RBS analysis sites of a ~420 nm thick partially filtered TiN thin film on Cr (~1000 nm thick) laser patterned at a fluence of 1.22 J/cm² using one, two and four pulses respectively. Laser patterning with one pulse has resulted in the selective removal of the TiN thin film with negligible damage to the Cr sacrificial layer. Laser patterning with two and four pulses has induced extensive thermal damage and cracking to the Cr sacrificial layer. This level of damage shows similarities to that shown by the micrographs in Figure 4.14(b and c), in which laser patterning was carried out using a slightly higher fluence of 1.60 J/cm² and a 20 μm test feature.
Figure 4.22 RBS sites of partially filtered TiN laser patterned at a fluence of 1.22 J/cm$^2$ using (a) one pulse (b) two pulses and (c) four pulses.

RBS was used to characterise the sites shown in Figure 4.22, with the obtained spectra shown in Figure 4.23. In particular, to characterise the damage to the Cr sacrificial layer. The three spectra indicate the presence of Cr films only on Si, as the leading edge of each spectrum corresponds to the backscattered energy of Cr. The spectrum obtained from the site laser patterned with one pulse shows the co-detection of Cr and Si. This is shown by the height of the spectrum around channel 95. It is unclear whether this is the result of thermal interaction induced by the laser pulse, or whether it is related to the spectrometer. The spectrum obtained from the site laser patterned with two pulses shows that relative to one pulse, there was a greater extent of co-detection between the Cr and the Si and is shown by the height of the spectrum around channel 85. This effect is also seen in the spectrum obtained after patterning with four pulses and is due to
thermal damage causing depth variation in the Cr sacrificial layer. Relative to the spectrum obtained from the site laser patterned with two pulses, the spectrum obtained after patterning with four pulses shows that the Cr film is slightly thinner. Gradual thinning of the Cr film is expected with increased number of pulses because the fluence 1.22 J/cm² used was above that required to ablate Cr, which is reported by Lee and Na [69] to be 0.31 J/cm².

Figure 4.23 RBS spectra (experimental) of partially filtered TiN on Cr on Si laser patterned at a fluence of 1.22 J/cm² using one, two and four pulses per area. The spectra show the presence of a Cr film only on Si, indicating the selective removal of the TiN thin film.

4.4.5 Role of Cr Sacrificial Layer Thickness

In order to determine the effect that thickness of the Cr layer has on the ablation of TiN thin film and the minimum desirable thickness of the Cr film, a sample with a Cr layer thickness of ~400 nm (while keeping the TiN film to a thickness of 420 nm) was patterned. Figure 4.24 shows a SEM micrograph of a TiN cantilever laser patterned at a fluence of 1.22 J/cm². EDS analysis (spectrum not shown) revealed the selective removal of the TiN thin film. From the image, it can be seen that the Cr sacrificial layer has not been damaged.
Figure 4.24 SEM micrograph showing a TiN cantilever laser patterned at a fluence of 1.22 J/cm², on a Cr layer (~400 nm thick) on Si showing that no damage has been induced to the Cr layer.

4.5 Laser Patterning of Preheated TiN on Cr Sacrificial Layer

Successfully depositing TiN thin films at room temperature to a thickness greater than 500 nm was difficult to achieve as films greater than this thickness cracked and usually underwent delamination. It is well known that stress in PVD films is proportional to film thickness, and therefore increasing the thickness will ultimately cause poorly adhered films to delaminate prematurely. This was observed and in order to improve the adhesion of the TiN the Cr/Si substrates were preheated to 200ºC.

RBS was used to analyse the composition of TiN deposited onto preheat Cr/Si substrates. Simulation of the obtained spectra (not shown) revealed the TiN stoichiometry to be TiN₁₀ with an uncertainty of ± 2.5%.

A partially filtered TiN thin film of thickness ~440 nm was deposited onto a Cr film (~500 nm thick) on Si. Figure 4.25(a and b) show SEM micrographs of sites laser patterned at a fluence of 1.53 J/cm² using one and two pulses. In both cases the TiN thin film was not selectively removed, however extensive cracking of the TiN was observed.
Figure 4.25 SEM micrographs of a ~440 nm thick TiN thin film on Cr laser patterned with a 20 μm feature at a fluence of 1.53 J/cm² using (a) one and (b) two pulses. Both micrographs show that the TiN thin film was not selectively removed.

In an attempt to selectively remove the TiN thin film, the number of pulses was increased to four while keeping the same fluence of 1.53 J/cm². The SEM micrograph of Figure 4.26 shows that the TiN thin film has been partially removed, however severe damage has been induced on the Cr sacrificial layer in the form of melting, pitting and cracking. It appears the TiN was removed as large chunks. This is evident from the cracking of the remaining, but irradiated, TiN thin film and the presence of large debris on the surface of the sample. Overall, the quality of patterning is poor and considered undesirable.
Figure 4.26 SEM micrograph of a ~440 nm thick TiN thin film on Cr laser patterned with a 20 μm feature at a fluence of 1.53 J/cm$^2$ using four pulses showing partial TiN thin film removal and severe damage induced on the Cr sacrificial layer.

Since the TiN thin film was not selectively removed using a single pulse and that single pulse patterning has been proven to provide the best quality patterning with minimal interference to the Cr sacrificial layer, the fluence was increased to higher levels. Figure 4.27(a-c) shows SEM micrographs of a ~380 nm thick partially filtered TiN thin film laser patterned at a fluence of 7.4 J/cm$^2$ using one, two and four pulses respectively. EDS analysis of the irradiated sites was carried out with the corresponding spectrum shown along side the respective micrograph.

Laser patterning with one pulse did not selectively remove the TiN thin film. The dominant Ti $K\alpha$ and Ti $K\beta$ peaks shown by the corresponding EDS spectrum indicates this. The micrograph shows that the TiN thin film has undergone extensive cracking and that the effect of the laser pulse has extended beyond the boundary of the projected feature. Laser patterning with two pulses did not selectively remove the TiN thin film either. The corresponding EDS spectrum shows dominant Ti $K\alpha$ and Ti $K\beta$ peaks, indicating the TiN remained. The micrograph shows that a second pulse induced melt-flow of the TiN. Melt-flow of this type is typically associated with the ablation of metal thin films. EDS analysis (spectrum not shown) of a wave-like droplet at the edge of the irradiated region indicated the material to be TiN. As with patterning with one pulse, a notable feature is the presence of large cracks in the laser irradiated region. The size of the cracks suggests that the underlying Cr layer also cracked. This seems likely as a
small section of cracked Cr film is visible at the edge of the patterned region and is highlighted by the white circle.

The micrograph of the site laser patterned with four pulses shows an increased level of melting. The corresponding EDS spectrum shows dominant Cr Kα and Cr Kβ and Cr L peaks. This indicates that the relative amount of TiN detected is less than that detected after laser patterning with two pulses. By examining each of the EDS spectra, it can be seen that the relative height of the Cr peaks increased with increased number of pulses. This information, coupled with the micrographs showing the melt-flow behaviour suggests that the TiN film became proportionally thinner with increased number of pulses.
Chapter 4 Laser Patterning of Partially Filtered TiN Thin Films

It is clear from the SEM micrographs presented as Figure 4.27(b and c) that attempting to selectively laser pattern the TiN film with more than one pulse (in this case two and four pulses) does not bring about the removal of the TiN thin film selectively from the underlying Cr film. Therefore, the use of RBS analysis to characterise the laser patterning of the same film will only be presented in the case for a single pulse per area at a fluence of 7.4 J/cm$^2$.

Figure 4.28(a and b) show RBS spectra of the same film in the deposited state and after laser patterning at a fluence of 7.4 J/cm$^2$ with one pulse per area respectively. RUMP simulation of the deposited TiN on Cr revealed a ~380 nm thick TiN thin film on ~1000 nm Cr. The spectrum of the RBS site laser patterned at a fluence of 7.4 J/cm$^2$ shows a similar shape to the spectrum of the deposited films, signifying that the TiN film remained on the surface of the Cr after irradiation with the laser pulse. However, two distinct differences between the two spectra must be addressed. The first difference is that the overall number of counts is less for the spectrum obtained from the site laser patterned at a fluence of 7.4 J/cm$^2$ compared to the spectrum obtained from the as deposited films. The second difference is that the peak around channel 275 for the spectrum obtained from the site laser patterned at a fluence of 7.4 J/cm$^2$ has a relatively lower number of counts compared to the spectrum of the as deposited film. Both of these differences are attributed to the detection of Si through cracks in the TiN and Cr films and in scattered regions were the TiN and Cr films were simultaneously removed.
from the Si substrate. The ensuing effect of exposed Si is a contribution in Si yield corresponding to the backscattered energy of Si, which has subsequently caused a reduction in the number of counts contributed by Ti and Cr. The effect of a relatively flatter peak around channel 275 is due to an intermediate layer of ~50 nm thickness that consists of TiN, Cr, O and Si. The presence of an intermediate layer is the result of cracking and delamination of the TiN and Cr films causing depth variations.

Figure 4.28 RBS spectra (experimental and simulated) of a ~380 nm thick partially filtered TiN thin film on Cr on Si in (a) the deposited state and (b) after laser patterning at a fluence of 7.4 J/cm² with one pulse per area.

One of the regions where TiN and Cr were simultaneously removed from the Si substrate is shown in the SEM micrograph of Figure 4.29(a), which was obtained within a site laser patterned at a fluence of 7.4 J/cm² using a single pulse. EDS analysis was carried out on the light and dark regions with the corresponding spectra shown as Figure 4.29(b and c). EDS revealed that the light regions consist of TiN on Cr on Si and the dark regions consist of Si only. The SEM micrograph shows extensive and severe cracking of the remaining TiN and it is this type of damage that suggest that the simultaneous removal of the TiN and Cr from the Si substrate occurred by some sort of shock-induced removal process caused by the high laser fluence. The fact that the TiN was not selectively removed from the Cr indicates that even for fluences of 7.4 J/cm² preheated TiN cannot be selectively removed from Cr.
This chapter reported the laser patterning of partially filtered TiN thin film from underlying materials of Si (100) substrate, and Cu and Cr sacrificial layers on Si. TiN thin films were irradiated using varying fluences in the range of 1.04 to 7.4 J/cm². TiN thin film deposited at room temperature showed selective removal from Si, Cu and Cr. The selective removal of TiN thin film from Cr sacrificial layer produced the best results when laser patterned with a single pulse. In this case the TiN thin film was ~420 nm thick on a ~1000 nm thick Cr layer. In contrast, it has been shown that a partially filtered TiN thin film deposited at 200°C cannot be selectively removed or patterned even at a fluence of 7.4 J/cm² using a single pulse.

Figure 4.29 (a) SEM micrograph of a ~380 nm thick partially filtered TiN thin film on Cr on Si laser patterned at a fluence of 7.4 J/cm² showing cracking of the TiN thin film and regions of exposed Si substrate (b) an EDS spectrum showing Ti, Cr and Si peaks (c) an EDS spectrum showing a Si peak only.
Chapter 5

Laser Patterning of Fully Filtered TiN Thin Films

This chapter presents the results of excimer laser micromachining of fully filtered TiN thin films deposited at 200ºC on Cr sacrificial layers. The quality of patterned features and selective removal of TiN was based on the same criterion as with the laser patterning of partially filtered TiN thin films. Parameters of laser fluence, number of pulses and TiN thin film thickness were varied to determine the best quality of patterning. Analytical techniques were used to characterise laser patterned sites and determine the extent of selective removal.

5.1 Characterisation of Fully Filtered TiN

Figure 5.1 shows a RBS spectrum of a fully filtered TiN thin film on Cr on Si. The spectrum shows an overlap in the Ti and Cr yields, which is represented by the peak around channel 280. A RUMP simulation of the spectrum revealed a ~360 nm thick TiN thin film deposited onto a 1000 nm Cr film on a Si substrate. RUMP simulations of the spectrum revealed the stoichiometry and uncertainty to be $\text{TiN}_{1.0 \pm 2.5\%}$. This means the stoichiometry of TiN deposited under fully filtered conditions was the same as that deposited under partially filtered conditions. Additionally, RUMP simulation revealed oxidation of the Cr at the TiN/Cr interface.
Chapter 5 Laser Patterning ofFully Filtered TiN Thin Films

Figure 5.1 RBS spectra (experimental and simulated) showing a ~360 nm thick TiN$_{1.0}$ film deposited under fully filtered conditions on Cr on Si.

The preferred orientation of the fully filtered films was investigated. Figure 5.2 shows an indexed XRD spectrum of a fully filtered TiN thin film deposited at 200°C onto Cr. The spectrum exhibits two TiN peaks; (111) at $2\theta = 42^\circ$ and (220) at $2\theta = 73.3^\circ$. The preferred orientation of fully filtered TiN is (220), which differs from the (111) preferred orientation exhibited by the partially filtered TiN.

Figure 5.2 XRD spectrum of showing TiN with a (220) preferred orientation.
As in the case of partially filtered TiN on Cr (as discussed in section 4.1), analysis of the interface of fully filtered TiN on Cr was also necessary in order to gain insight of the removal behaviour of the TiN. Figure 5.3 shows a SIMS spectra obtained from a ~360 nm thick TiN thin film on Cr. The thickness of the TiN/Cr interface was calculated by subtracting the depth at which the Cr spectrum starts to rise (~190 nm) from the depth that corresponds to the y-axis value of the Ti spectrum (~370 nm). In this case, the thickness of the TiN/Cr interface was estimated to be around 180 nm thick. This means the TiN/Cr interface for the fully filtered films was broader than the partially filtered TiN thin films, which were ~147 nm thick for the TiN deposited at room temperature and ~100 nm thick for the TiN deposited at 200ºC.

![Figure 5.3 SIMS spectra of TiN deposited under fully filtered conditions onto a Cr film showing the TiN/Cr interface to be approximately 180 nm thick.](image)

### 5.2 Laser Patterning of TiN Thin Films on Cr Sacrificial Layer

#### 5.2.1 Selective Removal of TiN Thin Film

Figure 5.4(a) shows a SEM micrograph of a ~255 nm thick fully filtered TiN thin film laser patterned using one pulse at a fluence of 2.03 J/cm². The feature is a 20 µm test pattern. An EDS spectrum obtained from analysing the patterned region is shown in Figure 5.4(b). The micrograph is labelled to highlight the exposed Cr and neighbouring non-irradiated TiN. The quality of pattern replication is high. However, the edge quality
is poor and inferior to that achieved for the partially filtered TiN thin film shown in figure 4.11. Cracks in the exposed Cr film can be seen (highlighted by the arrow), however this level of cracking is minimal and would not jeopardise the integrity of subsequent planar fabrication steps. The EDS spectrum clearly indicates the selective removal of the TiN by the absence of any peaks related to Ti. Moreover, the Cr peaks confirm the exposure of the Cr sacrificial layer.

![Figure 5.4 (a) SEM micrograph of a ~255 nm thick fully filtered TiN thin film on Cr laser patterned at a fluence of 2.03 J/cm$^2$ using a single pulse (b) EDS spectrum indicating an exposed Cr layer.](image)

Figure 5.4 (a) SEM micrograph of a ~255 nm thick fully filtered TiN thin film on Cr laser patterned at a fluence of 2.03 J/cm$^2$ using a single pulse (b) EDS spectrum indicating an exposed Cr layer.

Figure 5.5(a) shows a SEM micrograph of ~72 nm thick fully filtered TiN thin film on Cr on Si laser patterned at a fluence of 1.41 J/cm$^2$. The feature is a 20 μm test pattern. Figure 5.5(b) shows the corresponding EDS spectrum obtained from the patterned region. The EDS spectrum confirms the selective removal of the TiN thin film by the presence of the Cr peaks (Cr $L$, Cr $K\alpha$ and Cr $K\beta$) only. The quality of patterning is good with extremely high quality pattern replication. A noticeable feature is that the Cr film shows no damage, although some ablation debris is present on the surface of the exposed Cr. The TiN thin film shows some undesirable damage to the patterned edges.
5.2.2 Role of Laser Fluence on Patterning Quality

The role of laser fluence on patterning quality and selective removal of TiN was investigated by laser patterning a ~255 nm thick fully filtered TiN thin film deposited over a ~1000 nm thick Cr sacrificial layer. Laser patterning using a 20 μm test pattern was carried out at various fluence levels. Figure 5.6(a) shows a SEM micrograph of a site laser patterned at a fluence of 2.16 J/cm². EDS analysis (spectrum not shown) revealed that the TiN thin film was selectively removed from the Cr. The quality of pattern replication is high, however the edge quality is poor as ribbons of TiN are attached to the edges of the feature. Figure 5.6(b) shows a site laser patterned at a lower fluence of 2.03 J/cm². This site was discussed as Figure 5.4 and is included here for comparison purposes. The quality of pattern replication of the site in Figure 5.6(b) is not as good as that in Figure 5.6(a). The site in Figure 5.6(c) was patterned at a fluence of 1.22 J/cm². This value was near the ablation threshold of the TiN thin film. The edge quality and the replication quality are poor. The SEM micrograph in Figure 5.6(d) shows a site laser patterned at a fluence of 1.04 J/cm². At this fluence the TiN thin film was not selectively removed and the patterned region shows pitting and cracking of the TiN thin film.

Figure 5.5 (a) SEM micrograph of a ~72 nm thick fully filtered TiN thin film on Cr laser patterned with one pulse at a fluence of 1.41 J/cm² and (b) EDS spectrum obtained inside the laser patterned region.
Figure 5.6 SEM micrographs of a ~255 nm thick fully filtered TiN thin film on laser patterned using one pulse at fluences of (a) 2.16 J/cm$^2$ (b) 2.03 J/cm$^2$ (c) 1.22 J/cm$^2$ and (d) 1.04 J/cm$^2$ showing a reduction in patterning quality with decreasing fluence.

5.2.3 Laser Patterning near Ablation Threshold

The role of laser fluence near the ablation threshold was investigated by laser patterning fully filtered TiN thin films on Cr at varying fluences close to the ablation threshold. Figure 5.7 shows RBS spectra (experimental and simulated) obtained from a ~72 nm thick TiN on Cr in the as deposited state. The leading edge (channel 378) corresponds to the backscattered energy of Ti, confirming that a TiN thin film was present on the surface of the sample. The higher counts around channel 367 producing the peak near the Ti edge represent the overlap of the Ti and Cr yields. The peak is close to the leading edge because the TiN thin film is only tens of nanometers thick, i.e., ~72 nm.
The Cr edge has shifted to a lower energy from channel 386 to channel 370 due to attenuation of the backscattered yield caused by the TiN thin film.

![RBS spectra](image)

Figure 5.7 RBS spectra (experimental and simulated) of a ~72 nm thick fully filtered TiN thin film on Cr on Si in the as deposited state.

EDS and RBS analyses were carried out on the same ~72 nm TiN thin film to characterise laser patterned sites. Figure 5.8(a and b) show a SEM micrograph of the TiN thin film laser patterned using one pulse at a fluence of 0.725 J/cm$^2$ and a corresponding EDS spectrum obtained from the patterned region. The pattern is a 20 μm feature. The SEM micrograph shows that the quality of patterning is extremely poor, although EDS analysis indicated, by the presence of Cr peaks only, that TiN was selectively removed.
Figure 5.8 (a) SEM micrograph of a ~72 nm thick fully filtered TiN thin film laser patterned at a fluences of 0.725 J/cm$^2$ with one pulse (b) EDS spectrum indicating the presence of exposed Cr.

Figure 5.9(a and b) shows RBS spectra (experimental and simulated) obtained from the same ~72 nm thick TiN on Cr after laser patterning with one pulse per area at a fluence of 0.58 J/cm$^2$ and a corresponding SEM micrograph respectively. The leading edge of the spectra (channel 385) corresponds to the backscattered energy of Cr, suggesting that the TiN thin film was selectively removed. However, the shape of the spectrum does not represent the detection of only a Cr film (on Si), as was the case with the RBS spectrum of Figure 4.17 where the TiN thin film was completely removed. In fact, the shape differs through the presence of a small peak around channel 350. Simulation of the spectrum using RUMP revealed a 195 nm thick layer of TiN, Cr and O in the ratio 2:7:2 in the surface of the Cr sacrificial layer. The presence of TiN on the surface is confirmed by the SEM micrograph, which shows that the TiN thin film was only partially removed and that which remains is discontinuous over the surface of the Cr. The presence of residual TiN was due to the laser pulse being of an insufficient fluence to completely remove the film and the fact that a 195 nm layer of TiN, Cr and O was simulated is completely misleading and highlights a limitation in RBS analysis in relation to determining depth profiles when a significant depth variation exists.
Figure 5.9 (a) RBS spectra (experimental and simulated) of a ~72 nm thick fully filtered TiN thin film on Cr on Si laser patterned with one pulse per area at a fluence of 0.58 J/cm\(^2\) and (b) SEM micrograph of a region irradiated at 0.58 J/cm\(^2\) using one pulse showing incomplete removal of the TiN thin film.

Figure 5.10 shows RBS spectra (experimental and simulated) obtained from the same ~72 nm thick TiN on Cr after laser patterning with one pulse per area at a fluence of 1.22 J/cm\(^2\). At a higher fluence of 1.22 J/cm\(^2\), the RBS spectra indicated only the presence of Cr, suggesting the complete and selective removal of the TiN thin film.
The ablation threshold of the TiN varied depending on the size of the laser pattern features. The ablation threshold of the 20 μm feature was around 0.58 J/cm², while the ablation threshold of the 600 μm × 600 μm feature (used to pattern the RBS sites) was around 0.725 J/cm². This variation equates to an increase of approximately 25% and is most probably due to errors in the laser control system and the pyroelectric energy monitor used to calibrate the laser pulse energies.

The role of laser fluence near the ablation threshold was also investigated for a thicker TiN thin film. In this case, EDS and RBS analysis was carried out to characterise the laser ablation process.

Figure 5.11(a and b) shows a SEM micrograph of a ~360 nm thick TiN thin film patterned with one laser pulse at a fluence of 2.16 J/cm² and the EDS spectrum obtained from the patterned region. The minimum fluence required to pattern the TiN thin film using a single pulse was 1.04 J/cm². The large Cr peak at 5.41 keV (Cr Kα) indicates the presence of the Cr sacrificial layer. The Ti Kα peak indicates that residual TiN has remained on the surface of the Cr after laser patterning. Although the presence of residual TiN is undesirable in terms of a fabrication strategy, it appears that from the
SEM micrograph that the residual TiN is discontinuous over the surface of the Cr and would not pose as a barrier to a Cr sacrificial etch step, if required.

Figure 5.11 (a) SEM micrograph of a ~360 nm thick fully filtered TiN thin film laser patterned with one pulse at a fluence of 2.16 J/cm$^2$ (b) EDS spectrum of the laser patterned region showing the presence of TiN and dominant Cr peaks.

Further investigation of the same film was carried out at various fluence levels in order to gain information about the ablation behaviour of fully filtered TiN.

Figure 5.12(a-c) show SEM micrographs, together with corresponding EDS spectra, of the same ~360 nm thick TiN thin film laser patterned with a single pulse at fluences 0.87, 1.22 and 2.16 J/cm$^2$. Laser patterning at 0.87 J/cm$^2$ resulted in partial removal of the TiN, with the patterned region exhibiting a pitted morphology. The EDS spectrum shows the presence of Ti peaks, suggesting that TiN was detected. Laser patterning at fluences of 1.22 and 2.16 J/cm$^2$ also failed to selectively remove the TiN thin film from the Cr. By comparing the EDS spectra of all three sites it can be seen that as the laser fluence was increased, the intensity of the Ti signal decreased, suggesting that the amount of TiN removed increased with laser fluence. Roughness measurements of these three irradiated sites were measured in $R_a$ to be; 0.24 $\mu$m for the 0.87 J/cm$^2$ site and 0.06 $\mu$m for the 1.22 and 2.16 J/cm$^2$ sites.
Figure 5.12 SEM micrographs of a ~360 nm thick fully filtered TiN on Cr laser patterned using one pulse at fluences of (a) 0.87 J/cm$^2$ (b) 1.22 J/cm$^2$ and (c) 2.16 J/cm$^2$ with corresponding EDS spectra showing a reduction in the size of the Ti K$\alpha$ peak with increasing laser fluence.
In order to obtain information about the depth profile, RBS analysis was carried out on the same sites. Figure 5.13(a-e) shows the RBS (experimental and simulated) spectra obtained from the as deposited TiN thin film on Cr and after laser patterning at fluence levels of 0.87, 1.22 and 2.16 J/cm² respectively. Simulation of the spectrum corresponding to the as deposited sample revealed a ~360 nm thick TiN thin film on ~1000 nm Cr on Si substrate. Simulation of the spectra corresponding to laser patterning at 0.87, 1.22 and 2.16 J/cm² revealed the presence of TiN, Cr and O in varying compositional layers to depths of ~480 nm, ~240 nm and ~210 nm respectively. The presence of Cr on the surface of the roughened sites indicates that the residual TiN was present as a discontinuous layer over the Cr sacrificial layer. Although these values exceed the corresponding surface roughness values of 0.24 µm $R_a$ for the 0.87 J/cm² site and 0.06 µm $R_a$ for the 1.22 and 2.16 J/cm² sites, the results obtained from RBS analysis support the EDS analysis by revealing that the amount of TiN thin film removed increased with laser fluence.
Chapter 5 Laser Patterning of Fully Filtered TiN Thin Films

Figure 5.13 RBS spectra (experimental and simulated) of a ~360 nm thick fully filtered TiN thin film on Cr as deposited and laser patterned using one pulse per area at fluences of 0.87, 1.22 and 2.16 J/cm².

It must be noted that although RBS analysis can provide excellent composition information and depth profiling of planar layers, the overlapping in the Ti and Cr yields, coupled with the roughened laser patterned sites presenting depth variations to the incident beam posed difficulties in accurately simulating the spectra using RUMP. In light of this, the EDS and RBS analyses and obtained SEM micrographs revealed that the laser patterning TiN thin film at fluences close to the ablation threshold causes the TiN to not be completely removed. Moreover, the TiN will remain as discontinuous material on the surface of the underlying Cr.

5.2.4 Multiple-Pulse Patterning

Laser patterning a ~360 nm thick TiN thin film with a single pulse of 2.16 J/cm² did not result in the selective removal of the TiN. Hence, multiple pulse irradiations were tried. Figure 5.14 shows SEM micrographs of the same TiN thin film laser patterned at a fluence of 2.16 J/cm² using one, two, four and eight pulses. Figure 5.14(a) has been presented previously as Figure 5.11(a) and has been included in this set of images for comparison purposes only. Laser patterning with a second pulse induced melt-flow on the surface of the Cr. This amount of thermal damage is considered minimal and would
most likely not inhibit subsequent micromachining steps in a fabrication strategy. Laser patterning with four and eight pulses resulted in considerable damage to the Cr sacrificial layer and the surrounding TiN thin film. This level of damage is considered unacceptable.

Figure 5.14 SEM micrographs of a ~360 nm thick fully filtered TiN thin film laser patterned at a fluence of 2.16 J/cm² using (a) one pulse (b) two pulses (c) four pulses and (d) eight pulses. The micrographs show increasing thermal damage with number of pulses.

Since the TiN was not completely removed using a single pulse, EDS analysis was carried out on a site laser patterned at the same fluence (2.16 J/cm²) using two pulses. Figure 5.15(a and b) show a SEM micrograph and corresponding EDS spectrum. The presence of large Cr peaks and the absence of any Ti peaks indicate that the TiN has been completely removed from the Cr. The surface of the Cr shows fibre-like structures,
which are ridges caused by melt flow. Extensive cracking of the Cr layer can also be seen. The thermal damage around the edges of the laser patterned TiN feature is evident and considered undesirable.

Figure 5.15 (a) SEM micrograph of a ~360 nm thick fully filtered TiN thin film laser patterned at a fluence of 2.16 J/cm\(^2\) using two pulses (b) EDS spectrum of the patterned region indicating the detection of Cr only.

Figure 5.16 shows a SEM micrograph of the same TiN/Cr on Si laser patterned at a fluence of 1.22 J/cm\(^2\) using two pulses per area. It can be seen from the micrograph that the thermal induced damage to the edge of the patterned TiN thin film is not as severe as that shown in Figure 5.15(a). This shows that using a lower fluence with two pulses to selectively remove the TiN produces less thermal damage to the patterned TiN feature.

Figure 5.16 SEM micrograph of a ~360 nm thick fully filtered TiN thin film on Cr laser patterned at a fluence of 1.22 J/cm\(^2\) using two pulses.
Figure 5.17 presents a RBS spectra of the same ~360 nm thick TiN thin film on Cr laser patterned at a fluence of 1.22 J/cm$^2$ using two pulses per area. Laser patterning with two pulses has resulted in the TiN thin film being completely removed, as indicated by the shift in the leading edge of the spectrum to a higher energy that corresponds to Cr being detected on the surface. However, from the shape of the leading edge of the spectrum there appears to be some mixing of elements. Simulation of the spectrum using RUMP revealed only Cr and O on the surface of the Cr sacrificial layer.

Figure 5.17 RBS spectra (experimental and simulated) of ~360 nm thick fully filtered TiN on Cr laser patterned at a fluence of 1.22 J/cm$^2$ using two pulses per area.

Figure 5.18 shows SIMS spectra obtained after laser patterning with two pulses at a fluence of 1.22 J/cm$^2$. The detection of Cr indicated that the TiN layer has been completely removed. The spectra show that a very small amount of Ti has been detected to a depth of 5 nm. Extra O was detected on the surface of the Cr, which is due to oxidation of the Cr caused by the thermal impact of the second laser pulse.
5.2.5 Role of TiN Thin Film Thickness

The results show that the thickness of the TiN plays a role in the ablation threshold of the films and the quality of patterning obtained. The effect of TiN film thickness on ablation threshold was shown in the previous section with a ~72 nm thick TiN thin film having an ablation threshold of 0.725 J/cm$^2$ and a ~255 nm thick TiN thin film having an ablation threshold of 1.22 J/cm$^2$.

The role of TiN film thickness on the laser patterning quality and selective removal of TiN thin films from the Cr was investigated by laser patterning fully filtered TiN thin films of various thicknesses at a constant fluence using one pulse only. A fluence of 2.16 J/cm$^2$ was selected. Figure 5.19(a-d) shows SEM micrographs of laser patterned TiN thin films of thicknesses ~72 nm, ~255 nm, ~360 nm and ~700 nm. Figure 5.19(a) shows that the surface of the patterned site has nodule-like features. Also, the laser patterning extended beyond the boundary of the projected mask pattern and within this region only Cr was detected. EDS analysis was carried to determine the composition of the laser patterned surface. The obtained spectrum is shown in Figure 5.20(a). The Ti peaks indicate the presence of TiN. This result varied from the same film laser patterned at a reduced fluence of 1.41 J/cm$^2$ (Figure 5.5) in which the high quality selective patterning of the TiN thin film was observed. Figure 5.19(b) was presented previously as Figure 5.6(a) and showed selective removal of the TiN. Figure 5.19(c) was discussed...
previously as Figure 5.11(a) and showed that selective removal of the TiN was not achieved. Figure 5.19(d) shows poor quality patterning of the TiN thin film. EDS analysis indicated the selective removal of TiN from this site with the obtained spectrum shown in Figure 5.20(b).

Figure 5.19 SEM micrographs of fully filtered TiN thin films laser patterned at a fluence of 2.16 J/cm² and having thickness of (a) ~72 nm (b) ~255 nm (c) ~360 nm and (d) ~700 nm.

Figure 5.19 SEM micrographs of fully filtered TiN thin films laser patterned at a fluence of 2.16 J/cm² and having thickness of (a) ~72 nm (b) ~255 nm (c) ~360 nm and (d) ~700 nm.
The results obtained from laser patterning TiN thin films of different thicknesses at a fixed fluence and with one pulse show that the relationship between TiN thin film thickness and the ablation threshold of TiN is not straightforward. Of the TiN thin films that did show selective patterning of acceptable quality, the ablation threshold verses TiN thin film thickness was plotted and is shown in Figure 5.21. The graph shows that a linear relationship does not exist.

Figure 5.21 Graph of ablation threshold (J/cm$^2$) verses thickness (nm) for selectively patterned TiN thin film.

These investigations demonstrated that fully filtered TiN thin films will selectively pattern using excimer laser irradiation. At given fluences, fully filtered TiN thin films of
thickness ~72 to ~700 nm were selectively laser patterned using a single pulse. The results also showed that when TiN thin film thickness was ~360 nm, it was found to be difficult to achieve selective patterning of TiN even at a fluence of 2.16 J/cm$^2$. Instead of using a single pulse ablation, two pulses at a lower fluence enabled selective removal of the TiN thin film. For example, a fully filtered TiN thin film of ~360 nm thickness was removed selectively by two pulses at a fluence of 1.22 J/cm$^2$. However, the use of a second pulse resulted in damage of the underlying Cr layer.
Chapter 6

Wet-etch Patterning of TiN Thin Films and Cr Sacrificial Release

This chapter presents a novel strategy for wet-etch patterning and Cr sacrificial release of TiN structures. As with laser patterning, wet-etch patterning of TiN should facilitate the selective removal of TiN from the underlying material (substrate or sacrificial layer). Furthermore, in order to satisfying design requirements, it is desirable that patterned features be replicated with a high degree of edge quality. Underlying materials of Cu, Cr and Si were investigated to determine their etch selectivity to TiN. Determining the quality of patterned TiN involved evaluating pattern replication, edge quality of features, the degree of TiN removal and level of damage induce to the underlying material.

6.1 Selective Wet-etching of TiN

Wet-etching of TiN was carried out using SC-1 solution. A comprehensive literature search failed to bring up any prior publications on the wet-etch patterning of TiN and therefore it was necessary to first find a material to serve as a sacrificial layer to TiN. The effectiveness of SC-1 to etch TiN selectively was investigated by depositing TiN thin films using the filtered arc deposition system onto Si (100) substrate and onto Cu and Cr sacrificial layers. In the first instance, a visual inspection was used to determine whether the TiN thin film had been selectively removed following the wet-etching process. This was facilitated by the colour difference of the golden TiN varying sufficiently from the Si, Cu and Cr. When it was deemed that the TiN had been selectively removed, further investigation using analytical techniques was carried out.
Visual inspection showed that the TiN was etched from the Si substrate. When Cu was used as a sacrificial layer, the SC-1 removed the TiN but etched the Cu in an aggressive manner. Consequently, the use of Cu as a sacrificial layer for TiN was not pursued. Visual inspection revealed that TiN etched selectively from the Cr sacrificial layer. Furthermore, the absence of bubbles on the surface of the Cr or any discoloration of the Cr surface led to the assumption that the Cr did not appear to react with SC-1. As a result, the use of Cr as a sacrificial layer for TiN was pursued.

6.2 Wet-etching Compatibility of TiN with Cr Sacrificial Layer

As in previous studies, RBS was used to assess the extent to which TiN could be selectively etched. The technique was also used to determine the etch rate of the TiN by analysing TiN thin films prior to and after etching in SC-1 for various lengths of time. Figure 6.1 compares RBS spectra of partially filtered TiN on Cr prior to and after etching in SC-1 at room temperature for 40, 67 and 100 minutes. RUMP simulation on the as deposited film system revealed TiN and Cr film thicknesses of ~365 nm and ~515 nm respectively. Etching for 40 minutes resulted in the TiN thinning to ~125 nm. This equates to an etch rate of ~6 nm/min. The spectrum obtained after etching for 67 minutes shows that the leading edge has shifted from channel 368 to 378, indicating that the TiN was completely removed and the Cr sacrificial layer was exposed. The spectrum obtained after etching for 100 minutes is identical to that obtained after etching for 67 minutes. This means the SC-1 did not etch the Cr, even after a further immersion of 33 minutes.
Figure 6.1 RBS spectra of TiN on Cr on Si prior to and after etching in SC-1 for 40, 67 and 100 minutes. The spectra indicate that the TiN etched completely from the Cr using SC-1 at a rate of ~6 nm/min. The Cr sacrificial layer is not etched by the SC-1.

Figure 6.2 compares the RBS spectra of a ~223 nm thick film of Cr on Si prior to and after etching in SC-1 for 120 and 390 minutes. The spectra are virtually identical. This indicates that the Cr film was not etched over the time investigated. These results confirm the suitability of Cr as an etch resistant metal to SC-1 solution.
Chapter 6 Wet-etch Patterning of TiN Thin Films and Cr Sacrificial Release

Figure 6.2 RBS spectra of Cr on Si and after etching in SC-1 for 120 and 390 minutes. The likeness of the spectra indicates that the Cr was not etched in the SC-1 over the time investigated.

Establishing that TiN etches selectively from Cr and that SC-1 does not etch Cr is advantageous in terms of establishing a novel material combination for surface micromachining. However, determining the uniformity of TiN etching is also important as this can affect the quality of patterned features. Figure 6.3(a and b) shows a SEM micrograph of a partially filtered TiN thin film etched in SC-1 for a period of 40 minutes and a corresponding EDS spectrum. The presence of Ti peaks on the EDS spectrum indicates that TiN is present on the surface. The micrograph shows the presence of pitting in the TiN thin film. Pitting of this nature is initiated by the presence of pinholes in the TiN thin film, which has been exaggerated by etching the TiN with a SC-1 solution.
Figure 6.3 (a) SEM micrograph of partially filtered TiN etched in SC-1 for a period of 40 minutes and (b) EDS spectrum obtained from the highlighted region. The EDS spectrum indicated the presence of TiN.

Figure 6.4(a-c) show an SEM micrograph of a partially filtered TiN thin film etched in SC-1 for 63 minutes and two corresponding EDS scans taken from different regions on the sample surface (as indicated). The micrograph shows that further etching has increased the size of the pits. The EDS spectra indicate that the TiN has not been etched uniformly as a region of TiN on Cr and a region of Cr only have been detected. The premature exposure of the Cr sacrificial layer is due to the pits in the TiN thin film being etched and increasing in size.
Figure 6.4 (a) SEM micrograph of a partially filtered TiN etched in SC-1 for 63 minutes (b) EDS spectrum indicating the presence of TiN on Cr on Si (c) EDS spectrum indicating the presence of Cr on Si. (Both EDS spectra correspond to the labelled regions in Figure 6.4(a)).

Figure 6.5 shows a SEM micrograph of a partially filtered TiN thin film etched in SC-1 for 67 minutes 40 seconds and an EDS spectrum obtained from the highlighted region. The micrograph shows a smooth surface. In fact, the TiN thin film was completely removed to expose the Cr sacrificial layer. This is confirmed by the EDS spectrum which shows Cr and Si peaks only.

Figure 6.5 SEM micrograph of a partially filtered TiN thin film after etching in SC-1 for 67 minutes 40 seconds and a corresponding EDS spectrum indicating the presence of Cr on Si only.
6.3 Wet-etch Patterning of Fully Filtered TiN Thin Films on Cr Sacrificial Layer

As Cr proved suitably resistant to SC-1, the wet-etch patterning of TiN was investigated using Cr as the sacrificial layer. UV photolithography was used to create a mask on the surface of the TiN. Preliminary investigations showed that the photoresists AZ4620 and AZ1512 used were not suitably resistant to the SC-1 solution as both of these photoresists peeled-off in areas or were badly damaged. Consequently, the use of photoresist to mask TiN was abandoned. An alternative method was developed in which Cr was sputtered over the TiN to serve as a contact mask. The idea being that Cr serves as a sacrificial layer and a contact mask to provide the convenience of completely removing the contact mask (post TiN etching) when etching the sacrificial layer. This strategy would rely on the proviso that the CEP-200 used to etch the Cr would completely remove the Cr from the TiN and that the TiN would not be etched by the CEP-200.

Figure 6.6 shows a fractograph of the three-film system of Cr/TiN/Cr on Si used in strategy to wet-etch TiN thin film.

![Fractograph of Cr/TiN/Cr on Si](image)

Figure 6.6 SEM micrograph of a fractograph of the Cr/TiN/Cr on Si system used to wet-etch TiN thin film.

In order to determine the etch selectivity of Cr to TiN when etched in CEP-200, RBS was carried out on a film system of Cr/TiN/Cr on Si prior to and after etching in a CEP-200. Figure 6.7 shows three RBS spectra: Cr/TiN/Cr on Si; after etching in CEP-200 for 15 minutes; and after etching in a CEP-200 for 30 minutes. The Cr/TiN/Cr on Si spectrum shows that the leading edge corresponds to the backscattered energy of Cr.
Simulation of the spectrum using RUMP revealed the Cr contact mask layer to be ~223 nm thick. The spectrum obtained after etching for 15 minutes shows that the Cr contact mask layer is completely removed from the surface of the TiN. The resultant spectrum is typical of a TiN on Cr spectrum and shows that the signal corresponding to a Cr contact mask layer is now absent and that the leading edge of the spectrum corresponds to the backscattered energy of Ti (channel 368). The spectrum obtained after etching for 30 minutes is virtually identical to that obtained after etching for 15 minutes. This means that the thickness of the TiN remained the same and that the TiN was not etched by CEP-200, even when exposed for a period of greater than 15 minutes. This is more like ~28 minutes as the Cr contact mask layer etch rate was shown to be removed in around 2 minutes at an etch rate of approximately 200 nm/min.

Figure 6.7 RBS spectra of Cr/TiN/Cr on Si prior to and after etching in CEP-200 for 15 and 30 minutes. The spectra show that the Cr contact mask was etched from the TiN and that the TiN was not etched by the CEP-200 over the period investigated.

Figure 6.8(a) shows a SEM micrograph of a wet-etched patterned TiN thin film on Cr and with the Cr contact mask over the patterned TiN, i.e., Cr/TiN/Cr/Si. The feature is a 20 μm feature. The Cr contact mask was etched for ~1 minute to expose the TiN and the photoresist was stripped in acetone. The TiN was etched for 47 minutes. The EDS spectrum (Figure 6.8(b)) was taken from inside the patterned region and indicates that
the Cr sacrificial layer has been exposed. The absence of any peaks related to Ti indicates that the TiN was completely removed.

![a] Figure 6.8 (a) SEM micrograph of a wet-etched TiN thin film (20 μm feature) on Cr with the Cr contact mask over the patterned TiN and (b) EDS spectrum indicating the presence of the exposed Cr sacrificial layer.

### 6.4 Etching of Cr Sacrificial Layer

Figure 6.9(a-d) shows SEM micrographs of wet-etch patterned TiN thin film on Cr that has undergone etching of the Cr sacrificial layer. The TiN was deposited under fully filtered conditions. The features are 20, 15, 5 and 2.5 μm respectively. The micrograph of the 20 μm feature (Figure 6.9(a)) has been labelled to highlight the TiN regions and the adjoining regions of etched Cr sacrificial layer. The Cr sacrificial etch step had a duration of 4 minutes 50 seconds. It should be noted that Cr contact mask was completely removed from the TiN during the sacrificial etch step. The micrographs show that the TiN thin film exhibits pitting and that some of these pit are up to 4 μm across. These pits were mostly likely the result of SC-1 penetration through pinholes in the Cr contact mask or laterally driven etching through voids between the Cr mask and the TiN. Further optimisation of the process is required to minimise this effect. These micrographs highlight the effect of feature size on the quality of wet-etched TiN patterning. The 20 μm and 15 μm features show that the quality of pattern replication is good, however the edge quality is poor. The poor edge quality can be attributed to a lack of uniformity in etching of the columnar growth structure of the TiN thin film. The 5
µm and 2.5 µm features show that the quality of pattern replication has reduced as the feature size has reduced due to the effect of rounding at the ends of the features. This rounding effect was also observed in the case of laser patterned TiN features (see Figure 4.21(b-d)). Although the quality of the 2.5 µm feature is poor it is recognisable, whereas attempts made to laser pattern a 2.5 µm feature were unsuccessful (see Figure 4.21(e)). As with the laser patterned features, the wet-etched patterned features also showed that the quality of pattern replication is dependent on feature size.

Figure 6.9 SEM micrographs of wet-etch patterned TiN thin film features that underwent etching in CEP-200 to remove the Cr contact mask layer, with feature sizes (a) 20 µm and (b) 15 µm (c) 5 µm and (d) 2.5 µm.

Figure 6.10 shows an EDS spectrum obtained from the etched Cr sacrificial layer as shown highlighted in Figure 6.9(a). The presence of a small Cr peak indicates that the Cr sacrificial layer was not completely etched from the Si. In this case, the Cr sacrificial...
The TiN thin films that broke apart were deposited in the fully filtered mode. Partially filtered TiN thin films deposited at room temperature onto Cr were laser patterned (see chapter 4) and used to demonstrate the release of TiN structures through wet-etching of the Cr sacrificial layer. Features included 10 µm wide cantilevers and bridges of varying lengths. Figure 6.11 shows SEM micrographs of a laser patterned TiN bridge (length: 76 µm) that has undergone etching of the Cr sacrificial layer for 5 minutes 40 seconds. Figure 6.11(a) shows the entire bridge with supports and is labelled to highlight the TiN structure and exposed Si substrate. A noticeable feature of the structure is the presence of an uneven and pale discoloration along the length of the bridge and along the supports. The discoloration corresponded to regions of Cr that were not etched. The Cr was made visible through the TiN thin film by increasing the acceleration voltage of the SEM to 30 kV, which results in a electron/material interaction depth of around 5 µm. Figure 6.11(b) shows a higher magnification image where the bridge joins the support, which is labelled to show where the EDS analyses were carried out.
Figure 6.11 SEM micrographs of a laser patterned TiN bridge (length: 76 μm) showing (a) the entire feature and (b) the bottom bridge support.

Figure 6.12(a and b) show the obtained EDS spectra. Figure 6.12(a) indicates that TiN, Cr and Si were detected. Figure 6.12(b) corresponds to the area where the Cr sacrificial layer is not visible through the TiN and the spectra indicate that the Cr has been etched.

Figure 6.12 EDS spectra obtained from highlighted regions shown in figure 10(b). The spectra are of areas with the (a) Cr sacrificial layer and (b) TiN only.

In order to completely undercut TiN structures, the Cr etch time was increased from 5 minutes 40 seconds to 9 minutes. Figure 6.13(a) shows SEM micrographs of a TiN bridge (length: 82 μm) that has had the Cr sacrificial layer etched to release the TiN in some regions. The micrograph shows that the Cr still remains and supports the TiN, whereas in other areas the Cr has been etched and no longer provides support for the
TiN structure. It is these regions where large sections of the TiN bridge (and support) have broken away. Figure 6.13(b) shows a higher magnification micrograph of the same feature highlighted by the white rectangle in Figure 6.13(a). The micrograph shows where TiN has become detached and also shows the presence of large cracks in the TiN thin film, which are most likely the cause of the sections breaking away from the feature. Since it has been shown using RBS that TiN is not etched by the CEP-200, it is assumed that the TiN structures broke apart due to the presence of cracks induced by the laser pulse.

A wet-etch strategy for patterning and releasing TiN features on Cr sacrificial layers has been developed. TiN thin films were wet-etch patterned using a SC-1 solution. Sputtered Cr films were used as both the sacrificial layer and contact mask layer and were etched in CEP-200. RBS was used to show that etch selectivity exists between TiN and Cr when exposed to their respective etchant. This confirmed the suitability of Cr as a sacrificial layer in a micromachining strategy for wet-etch patterning and releasing TiN thin films. Wet-etched TiN structures were released by etching the Cr sacrificial layer, however, all released structures broke apart. As an alternative, excimer laser patterned TiN structures had their Cr sacrificial layers etched. As a result, a semi-freestanding TiN bridge was realised.
Chapter 7

Discussion

One of the major outcomes of this investigation has been the demonstration of selective laser patterning of TiN thin films. However, the ability to achieve selective patterning of the TiN was observed to vary with arc deposition conditions, laser processing parameters and the choice of material underlying the TiN. The results are discussed in relation to thin film ablation mechanisms, type of macroparticle filtering, preferred orientation and residual stress.

7.1 Thin Film Ablation Mechanisms

Partially filtered TiN thin films deposited at room temperature were selectively ablated from Cr and Cu in a single pulse. Such ablation behaviour is consistent with the explosion mechanism proposed by Zaleckas and Koo [77]. They concluded that whenever the evaporation or decomposition temperature of a substrate is lower than the melting temperature of the film, a positive pressure develops under the film causing explosive removal of the film. In the present case, the melting point of TiN (2930ºC) is higher than the evaporation or boiling temperature of both Cr (2671ºC) and Cu (2562ºC), as shown in Table 7.1. Hence, the explosion mechanism could be considered pertinent as a means of characterising the removal of TiN thin film from Cr or Cu.

The selective ablation of TiN thin film from Si was achieved after eight pulses. The removal of TiN from Si occurred by a process of crack propagation and eventual delamination with increasing number of pulses. This form of removal is not characteristic of the explosion mechanism. Since to the evaporation or boiling temperature of Si (3265ºC) exceeds the melting temperature of the TiN (2930ºC) the explosion mechanism cannot be considered applicable. The characteristics of crack
propagation and eventual delamination with increasing number of pulses shown by the removal of TiN from Si were similar to the removal mechanism reported by Schubert and coworkers [73] for the removal of 3 μm thick TiN thin films from tool steel using 4 to 20 excimer laser pulses. Since the evaporation or boiling temperature of tool steel (note: approximately 2750ºC for Fe) is lower than the melting temperature of TiN (2930ºC), one would have expected the explosive removal of the TiN thin film in a single pulse to be observed. It is the opinion of this author that explosive removal did not occur because the 3 μm TiN thin films used were too thick.

It should be noted that partially filtered TiN thin films deposited at 200ºC were not selectively removed from Cr sacrificial layers in a single pulse, even when irradiation was carried out at a maximum fluence of 7.4 J/cm². However, at this fluence the ablation of TiN was observed and showed melt-flow characteristics. It was observed that fully filtered TiN thin films (which were all deposited at 200ºC) over a range of thicknesses of ~75 to ~700 nm could be selectively removed from Cr. As in the example of partially filtered TiN deposited at room temperature, the experimental observations were consistent with removal by the explosion mechanism.

The vaporisation model [50] and two-phase model [78] were discounted as possible mechanisms to account for the single pulse selective removal of both partially filtered TiN deposited at room temperature and fully filtered TiN because the edges of the laser patterned TiN features showed no signs of melting, a phenomenon that would have been expected if these ablation mechanisms were applicable.

7.2 Effect of Underlying Materials

In order to assess the role that the underlying materials could have on the laser ablation process it is first necessary to discuss the interaction of a laser pulse with the film/substrate system. It is worth reiterating that thin film ablation by the explosion mechanism is dependant upon the decomposition or boiling temperature of the underlying material being lower than the melting point of the thin film material [77]. This has been shown to be the case for the laser ablation of TiN from both Cr and Cu sacrificial layers. Although the boiling points of Cr and Cu are very close at 2671ºC and 2562ºC, the damage induced by the laser when selectively patterning TiN film from Cr sacrificial layer is considered negligible compared to the damage incurred by the Cu sacrificial layer. Depth profiling carried out using SIMS showed that O was present on
the surface of the Cr and Cu. This is of particular interest when considering TiN on Cr, as CrO\textsubscript{x} based compounds are highly volatile. The compound CrO\textsubscript{2} decomposes at a temperature of 300\textdegree{}C \cite{118}. The presence of CrO\textsubscript{2} on the surface of the Cr sacrificial layer could account for reduced damage to the surface of the Cr sacrificial layer. In the case of an oxide layer on the Cu, compounds such as Cu\textsubscript{2}O and CuO are not expected to play a significant role in the explosion mechanism as they have boiling points comparable to that of Cu \cite{119}.

It is clear from discussion by both Metev and Veiko \cite{51} and Tóth and coworkers \cite{66} that large differences in the thermal expansion coefficients between the film and substrate can result in additional stresses being induced at the film/substrate interface during irradiation with a laser. The additional stress could ultimately result in the development of microcracks, which in turn propagate and lead to film ablation.

The results showed that the quality of patterning of TiN thin film depended significantly upon the underlying material (Cr or Cu). TiN on Cu showed poor quality laser patterned features, while TiN on Cr resulted in high quality laser patterned features. The difference in laser patterning quality is probably due to the difference in the thermal conductivity between Cr and Cu, which is reported as 67 and 398 Wm\textsuperscript{-1}K\textsuperscript{-1} respectively.

The high thermal conductivity of Cu resulted in the thermal energy induced by the laser pulse and transmitted through the TiN thin film to be dissipated more readily and therefore gave rise to laser patterned features that are heavily rounded at the corners. In the case of Cr as the sacrificial layer, the thermal energy was dissipated more slowly (more so than in the case of Cu) and therefore resulted in laser patterning of a higher quality.

Table 7.1 lists physical properties of materials relevant to this study.
Table 7.1 Physical properties of materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Melting Point (°C)</th>
<th>Boiling Point (°C)</th>
<th>Thermal Coefficient Expansion (10⁻⁶/K)</th>
<th>Thermal Conductivity (W/m/K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiN</td>
<td>2930</td>
<td>-</td>
<td>9.4</td>
<td>19</td>
</tr>
<tr>
<td>Cr</td>
<td>1907</td>
<td>2671</td>
<td>6.2</td>
<td>67</td>
</tr>
<tr>
<td>CrO₂</td>
<td>-</td>
<td>300⁺</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Cu</td>
<td>1085</td>
<td>2562</td>
<td>16.5</td>
<td>398</td>
</tr>
<tr>
<td>Cu₂O</td>
<td>1235⁺</td>
<td>1800⁺</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CuO</td>
<td>1326⁺</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Ti</td>
<td>1668</td>
<td>3287</td>
<td>8.4</td>
<td>11.4</td>
</tr>
<tr>
<td>Si</td>
<td>1414</td>
<td>3265</td>
<td>2.6</td>
<td>156</td>
</tr>
</tbody>
</table>

*From [118]. *From [119].

7.3 Effect of TiN Deposition Conditions on Laser Patterning

It is clear from the results that the mode of macroparticle filtration and the deposition temperature had a significant effect on the ablation behaviour. This is most evident when comparing two TiN thin films of comparable thickness; a ~360 nm fully filtered TiN selectively laser patterned at a fluence of 2.16 J/cm², and a ~380 nm partially filtered TiN which could not be selectively laser patterned, even at fluences up to of 7.4 J/cm². Such significant differences in response when trying to laser ablate show that the mode of filtering affects the characteristics of the TiN thin films in a manner that influences the way in which TiN is laser ablated. Two factors that could have contributed to this outcome are, one, the difference in the number of macroparticles in the films, and two, observed differences in the microstructure of the TiN.

Figure 7.1(a and b) show SEM micrographs of TiN thin films deposited onto Cr sacrificial layers under partially filtered and fully filtered modes respectively. The micrographs show, as one would expect, a greater number of macroparticles per unit area for the partially filtered TiN than the fully filtered TiN. The presence of macroparticles is rejected as a reason of accounting for differences in the ablation threshold of TiN as their numbers are insufficient. Furthermore, in tool coating applications, the presence of macroparticles at the substrate/coating interface degrades
the tribological performance of coatings by reducing adhesion and rendering them more prone to delamination [31], [32]. If an analogy is drawn between the ability to ablate TiN thin film and the tribological performance of TiN tool coatings, then the partially filtered TiN thin film should have been laser ablated at a fluence level below that required to laser ablate the fully filtered TiN thin film. This was not observed.

![SEM micrographs of TiN thin films deposited using cathodic arc evaporation with different modes of filtering](image)

(a) Partially Filtered TiN  
(b) Fully Filtered TiN

Figure 7.1 SEM micrographs of TiN thin films deposited using cathodic arc evaporation with different modes of filtering (a) partially filtered TiN and (b) fully filtered TiN. The micrographs show that the number of macroparticles per unit area is greater for the partially filtered TiN than the fully filtered TiN.

Having rejected the first possibility relating to the number of macroparticles, we now need to consider the possible influence of the microstructure of TiN as a function of the filtration mode and the deposition temperature.

The structure of the TiN thin films was examined using XRD analysis. Figure 7.2(a and b) show XRD spectra obtained from a partially filtered TiN thin film on Cr and a fully filtered TiN thin film on Cr respectively. Both TiN thin films were deposited at 200ºC and had comparable thicknesses of ~380 nm for the partially filtered TiN thin film and ~360 nm for the fully filtered TiN thin film. It must be noted that the intensity (y-axis) scale of the two XRD spectra differs by a factor of 10. The most striking feature is that the partially filtered TiN exhibits a strong (111) preferred orientation while the fully filtered TiN exhibits a (220) preferred orientation. Additionally, the fully filtered TiN exhibits a small but recognisable (111) peak. Dashed lines have been superimposed to represent the diffracting angle, 2θ, of the TiN (111) and TiN (220) planes in a stress-free state, \( d_0 \), as report in powder diffraction files [120].
Figure 7.2 XRD spectra of partially filtered and fully filtered TiN thin films deposited at 200°C showing (a) partially filtered TiN with a (111) preferred orientation and (b) fully filtered TiN with a (220) preferred orientation. The dashed lines represent the planar spacing, $d_0$, for the TiN (111) and (220) orientations in a stress-free state.

It is possible to interpret the respective XRD spectra in relation to residual stress. Two characteristics of an XRD spectrum can provide an indication of residual stress: one, the location of peaks in terms of the diffracting angle, $2\theta$, and two, the shape of the peaks. With respect to peak location, Bragg’s Law (equation (13), in chapter 3) shows that diffraction angles smaller than those corresponding to the stress-free state $d_0$, the greater
the d-spacing. An increase in the d-spacing indicates a laterally compressed lattice, which translates to compressive stress. The relationship between an increased d-spacing and lateral compressive stress is governed by the theory of elastic behaviour. The elastic relationship between stress and strain is given by Young’s modulus, represented as:

\[ E = \frac{\sigma}{\varepsilon} \]  

(15)

where \( \sigma \) is the stress and \( \varepsilon \) is the strain. Any laterally induced strain will cause transverse strain by the elastic constant, Poisson’s ratio, which is represented as:

\[ \nu = -\frac{\varepsilon_y}{\varepsilon_z} \]  

(16)

where \( \varepsilon_y \) and \( \varepsilon_z \) is the strain in the y and z directions respectively [121]. Thin films are considered stress-free in the z-axis, therefore, when a crystal is under compression the lattice is only compressed laterally to the surface. Because crystals exhibit elastic behaviour, any lateral compression will cause tensile strain in the z-axis resulting in an increase in the d-spacing of the crystal planes parallel to the surface i.e., the planes reflecting the X-rays.

The shape of an XRD peak is related to the defect density and the level of strain imposed on the lattice [122]. The peak representing the (111) preferred orientation of the partially filtered TiN (see Figure 7.2(a)) is narrow and high in intensity, which signifies a crystal structure with low defect density. The peak representing the (220) peak of the fully filtered TiN (see Figure 7.2(b)) is broad and low in intensity, which is indicative of a lattice with a high number of defects and strain [122]. In addition, both the (111) peak of the partially filtered TiN and fully filtered TiN and the (220) peak of the fully filtered TiN have shifted to smaller diffraction angles than that represented by stress-free TiN. This signifies the presence of compressive stress. Furthermore, both the (111) and (220) peaks of the fully filtered TiN have shifted to a smaller diffraction angle than the (111) peak of the partially filtered TiN. This signifies that the fully filtered TiN exhibited higher compressive stress than the TiN thin film deposited under partially filtered conditions. Konyashin and coworkers [32] investigated the difference in
cathodic arc evaporated TiN thin films when deposited with and without a ¼ torus filter. They reported that the filtered TiN had higher compressive stress (3.3 GPa) compared with the unfiltered TiN (1.7 GPa).

Quantifying the absolute stress in TiN thin films was beyond the scope of this study. However, using XRD analysis it is possible to relate the compressive stress of the partially filtered deposited at 200°C to the fully filtered TiN. This is achieved by determining the diffraction angle of the same peaks, in this case the (111) peak, for both the partially filtered TiN and the fully filtered and substituting the values into Bragg’s Law (equation 13, chapter 3) to determine the respective d-spacings. By combining equations (15) and (16), and representing the strain component as lattice deformation the following equation is presented [102];

\[
\sigma = \frac{E(d_0 - d)}{\nu d_0}
\]  

(17)

where \( E \) is Young’s modulus, \( \nu \) is Poisson’s ratio, \( d_0 \) is the stress-free d-spacing. Furthermore, it is possible to interrelate the compressive stress in the two different thin films by means of a ratio, or stress factor, \( S.F. \):

\[
S.F. = \frac{\sigma_1}{\sigma_2} = \frac{d_0 - d_1}{d_0 - d_2}
\]

(18)

where subscript 1 represents the fully filtered TiN and subscript 2 represents the partially filtered TiN deposited at a temperature of 200°C. By determining the stress factor, \( S.F. \), the fully filtered TiN exhibited 1.7 times the compressive stress of the partially filtered TiN deposited at a temperature of 200°C. A reduced level of compressive stress and an improvement in the crystalline properties of a thin film are analogous with stress relieving. Hence, as observed, partially filtered TiN thin film deposited at 200°C is less likely to be selectively laser ablated with a single pulse since the film is less stressed and therefore less prone to removal by a process that has a stress-induced failure component like the one proposed by Tóth and coworkers [66]. In fact, results in section 4.5 showed that partially filtered TiN deposited at a temperature of 200°C did not undergo selective laser patterning. Conversely, it has been shown in
section 5.2 that fully filtered TiN was selectively laser patterned using a single pulse. From these results, it is the opinion of this author that the increased level of compressive stress in the fully filtered TiN facilitated the selective laser ablation of the fully filtered TiN thin films using a single pulse. Furthermore, it is entirely plausible that the single pulse selective laser ablation of fully filtered TiN thin film was attributed by the laser pulse inducing thermal expansion of the TiN, thus increasing the compressive stress and causing the film to be removed by stress induced failure and not by the explosion mechanism as discussed in section 7.1. The temperature at which the substrates were preheated resulted in differences in the laser ablation behaviour of partially filtered TiN thin films. TiN thin films deposited at room temperature exhibited selective patterning at a fluence of $1.22 \text{ J/cm}^2$, whereas, and as mentioned previously, TiN thin films deposited at $200^\circ\text{C}$ did not show selective removal, even for fluences up to $7.4 \text{ J/cm}^2$. Figure 7.3 shows the indexed XRD spectra of TiN deposited onto Cr at room temperature and $200^\circ\text{C}$. The dashed line represents the planar spacing, $d_0$, for the TiN (111) orientations in a stress-free state. Both spectra indicate a TiN (111) preferred orientation, although the two corresponding peaks show different intensities. This phenomenon is similar to that observed by Cheng and coworkers [122]. They reported an increase in the (111) peak intensities of filtered arc deposited TiN when the temperature of deposition was increased from $50^\circ\text{C}$ to $450^\circ\text{C}$. Furthermore, they reported that the reason for the increase in peak intensity with temperature might indicate a decrease in defect density and an improvement in the crystalline properties of the film.
Chapter 7 Discussion

Figure 7.3 XRD spectra of partially filtered TiN deposited at room temperature and 200°C. Both spectra show the TiN with (111) preferred orientation. The dashed line represents the planar spacing, $d_0$, for the TiN (111) orientations in a stress-free state.

A feature of the XRD spectra shown in Figure 7.3 is that both the TiN (111) peaks are located at $2\theta$ values that correspond to smaller diffraction angles than the stress-free reflection angle. This indicates the existence of compressive stress in both TiN thin films. Furthermore, the TiN thin film deposited at room temperature shows a greater deviation from the stress-free state than that of the film deposited at 200°C. This signifies that the TiN thin film deposited at room temperature is in a higher compressive state. Interestingly, Cheng and coworkers [122] reported that the internal compressive stress of the TiN deposited at a temperature of 50°C was 9.88 GPa, which reduced to 4.30 GPa when the TiN was deposited at 450°C. This means the TiN they deposited at a temperature of 50°C exhibited 2.3 times the stress of the TiN they deposited at a temperature of 450°C. By determining the stress factor, $S.F.$ (using equation (18)), the TiN deposited at room temperature exhibited 2.2 times the compressive stress of the TiN deposited at a temperature of 200°C, which is very similar to the value of 2.3 interrelating the two forms of TiN (deposited at 50°C and 450°C) investigated by Cheng and coworkers [122].

In regards to information gained from the XRD spectrum, the TiN deposited at room temperature exhibited inferior crystalline properties and a 220% increase in compressive
stress over TiN deposited at a temperature of 200°C. Interestingly, the TiN deposited at room temperature was selectively laser ablated using a single pulse, whereas the TiN deposited at a temperature of 200°C was not selectively removed. In view of these results, it is entirely plausible that like the fully filtered TiN the single-pulse selective laser ablation of partially filtered TiN thin film deposited at room temperature was also attributed to stress induced failure.

The selective removal of TiN thin films from Cr by a stress induced failure is supported by the investigations carried out on the interface of the partially filtered TiN deposited at room temperature and 200°C and the fully filtered TiN deposited at 200°C. The two types of TiN thin films that underwent selective laser ablation from the Cr had thicker interfaces, which may have been caused by the formation of a depth variation in the sputtered SIMS crater from the presentation of voids at the interface. The presence of voids indicates that the interface would be more susceptible to a stress induced failure due to having less continuous contact than that of a narrower and more densely contacted and continuous interface.

7.4 Wet-etch Patterning of TiN Thin Films and Cr Sacrificial Release

Laser micromachining TiN thin films on Cr sacrificial layers and etching the Cr sacrificial with CEP-200 micro-chrome etchant resulted in the TiN structures breaking apart. To determine if the laser pulse caused damage to the patterned TiN structures a wet-etching strategy was developed so that TiN structures could be released without the percussive shock associated with the pulsed ablation.

The results showed that the quality of laser patterned TiN and the wet-etch patterning TiN thin film were similar. Etching the sacrificial layer of the wet-etch patterned TiN thin film also resulted in the structures breaking apart. Although the wet-etch patterned TiN thin films showed the presence of etch pits, it is unlikely that the pits are the sole cause of the break up of the TiN thin film when the Cr layer was sacrificially etched. It is probable that the reason for the structures breaking is due to the release of strain energy enabling the propagation of crack in the film that were otherwise restricted from propagation by the support of the Cr sacrificial layer.

Attempts to release TiN stress structures using a sacrificial wet-etching method proved unsuccessful. However, during the course of laser micromachining test patterns into a
fully filtered TiN thin film on a Cr sacrificial layer some test structures in the form of TiN cantilevers became detached from the Cr layer. These cantilevers facilitated the determination of the stress gradient in the TiN thin film and are described in the next section.

7.5 Stress Gradient Characterisation of TiN Thin Film

When introducing a novel material combination or processing strategy for surface micromachining, it is crucial that the stress behaviour of the structural film be determined [85], [93]. In this investigation, the patterning of arc-deposited TiN thin films is novel and the selective patterning of TiN thin films using an excimer laser and wet-etching is novel. Therefore, for the realisation of TiN as a versatile structural MEMS material, it is fitting that an understanding of the stress behaviour of TiN thin film is obtained. In particular, the gradient stress as this causes undesirable out-of-plane bending of released structures [105]. One method of determining the gradient stress in a thin film is to fabricate a freestanding cantilever using micromachining techniques. However, the fabrication of TiN cantilevers in this work has been difficult due to the tendency of the released film to crack and fracture.

Figure 7.4 shows SEM micrographs of TiN cantilevers on a Cr sacrificial layer. The images show laser patterned TiN cantilevers that became detached and raised from the surface of the Cr. Although the deflection of the cantilevers has been restricted to zero, the downward bending nature of the cantilevers represents gradient stress in the TiN thin film, which is increasing compressive stress with film thickness.
Boutry and coworkers [81] reported that when cantilevers are released from the substrate the resulting stress relaxation leads to flat cantilevers if the initial film stress was homogeneous. When the deposited film has an initial depth stress gradient with an odd symmetry with respect to the mid-plane, the cantilever displays an upward or downward parabolic shape. For a linear in depth stress variation \( \frac{\delta \sigma_f}{\delta z} = \text{constant} \) the cantilever deflection magnitude \( \delta \) at distance \( L \) from the clamped end is given by:

\[
\delta = \left( \frac{1 - \nu_f}{2E_f} \right) L^2 \left( \frac{\delta \sigma_f}{\delta z} \right)
\]

where \( L \) is the distance from the clamped end and \( E_f \) and \( \nu_f \) are the Young’s modulus and Poisson’s ratio of the cantilever material. Due to the restriction in the tip deflection, it is not possible to quantitatively determine the stress gradient of the cantilevers in Figure 7.4 using equation (19). However, one of the cantilevers sits approximately 14 \( \mu \text{m} \) above the Cr sacrificial layer with a total deflected length of around 160 \( \mu \text{m} \). If the shape of the cantilever is considered as an arc, as shown by the schematics in Figure 7.5(a and b), then the radius of the arc is determined to be approximately 235 \( \mu \text{m} \). This means that if the tip of the cantilever were unrestricted, it would deflect downwards about 50 \( \mu \text{m} \).
Figure 7.5 Schematic showing an x-y plane view of a cantilever (a) restricted in the z-axis and (b) deflected approximately 50 \( \mu \text{m} \) downwards.

By applying equation (19), it is estimated that the TiN thin film has a gradient stress, \( \delta \sigma / \delta z \), of approximately 3.6 GPa/\( \mu \text{m} \). A gradient stress of this magnitude is considered extremely high compared with values of around 10's of MPa/\( \mu \text{m} \) desired for surface micromachined device that contain planar freestanding structures [81].
Chapter 8

Conclusions and Suggestions for Future Work

The conclusions of this work are summarised as follows:

It has been demonstrated that partially filtered TiN thin films deposited at room temperature can be selectively laser ablated with a single pulse using an excimer laser at 248 nm. In this case, Cr and Cu were used as sacrificial layers. The ablation of TiN thin film from Cr and Cu is consistent with the explosion mechanism of thin film removal proposed by Zaleckas and Koo [77]. The quality of TiN laser patterning was assessed in terms of edge quality, pattern replication and damage induced to the sacrificial layer. It was demonstrated that for all three of these criteria the use Cr as the sacrificial layer facilitated a better quality patterning than when Cu was utilised as the sacrificial layer.

Selective laser ablation of fully filtered TiN thin films was also demonstrated. It must be noted that all the fully filtered TiN thin films were deposited at a temperature of 200°C.

Partially filtered TiN thin films deposited at 200°C did not undergo selective laser ablation in a single pulse. However, the ablation of TiN was observed and showed melt-flow characteristics. This result is inconsistent with the explosion mechanism and therefore a conclusion is drawn that no single ablation mechanism can be applied to the ablation of TiN thin films.
Investigation using XRD analysis of the three types of deposited TiN revealed compressive stress. In the two cases where TiN thin films were selectively ablated, representative XRD spectra showed increased compressive stress over the TiN that did not undergo selective laser ablation. Although the ablation behaviour of TiN thin films from Cr and Cu sacrificial layers is consistent with the explosion mechanism of removal, it was observed that a relationship exists between increased compressive stress and the ability to selectively laser pattern TiN thin film. Therefore, it is concluded that the ablation process of TiN thin films is assisted by stress induced failure, which is caused by a further increase in the compressive stress induced by the interaction of the laser pulse and the irradiated material.

Since it was demonstrated that it was not possible to laser ablate partially filtered TiN thin films deposited at 200ºC, a novel strategy for wet-etch patterning TiN thin films was developed. Within this strategy it was demonstrated practically and confirmed using RBS analysis that TiN and Cr can be selectively removed from one another with the use of their respective etchants; SC-1 solution for etching TiN and CEP-200 micro-chrome for etching Cr. It is concluded that TiN and Cr can be used as a complementary material combination for surface micromachining. Furthermore, it was discovered that TiN and Cu are not a complementary material combination as Cu was observed to etch violently in the SC-1.

The discovery that CEP-200 micro-chrome etches Cr selectively from TiN facilitated the sacrificial release of both laser patterned and wet-etch patterned TiN stress-measuring structures. Undercut TiN structures were demonstrated, however, when completely under-etched the structures broke apart and could not be used to quantify the stress behaviour in the TiN. An estimation of the gradient stress in the TiN was made possible by TiN cantilevers becoming detached from the Cr sacrificial layer. A released cantilever, although its deflection was restricted in the z-axis, facilitated an approximate determination of the gradient stress in a fully filtered TiN thin film deposited at 200ºC. By approximating that the released cantilever adopted an arc-like shape, and by applying an equation that relates the deflection of a cantilever to gradient stress (equation (19)), it has been estimated that the gradient stress in a fully filtered TiN thin film is approximately 3.6 GPa/µm. From this information, it is concluded that fully
filtered TiN thin films have extremely high gradient stress levels and would therefore be limited in application as structural layers in surface micromachined MEMS.

Suggestions for future work are as follows:

Since the novel strategies of excimer laser micromachining and wet-etch patterning TiN thin film on Cr sacrificial layer have been demonstrated, future research could be carried out to apply this strategy to the fabrication of a functional MEMS device. In doing this it would be crucial to incorporate a design strategy that would minimise the impact of the gradient stress in the TiN, or alternatively, utilise deposition techniques or post-deposition annealing that reduce the residual stress in the TiN.

Due to its high hardness, TiN is widely exploited as a wear resistant coating on tools. Future research could be centred on depositing TiN onto micromachined components to provide a wear resistant layer. This would increase the operational lifetime of mechanical components. In doing this, it is probable that thicker TiN thin films will need to be selectively patterned from a range of materials; Nickel and Permalloy in the case of LIGA structures and polysilicon in the case of surface micromachined structures. Developing strategies to fulfil these requires would be considered important to the immediate success of TiN as a MEMS material.
References


[40] KÖHLER, M., “Etching in Microsystems”, WILEY-VCH, 1999, Page 331


References


References


References


References


[120] Powder diffraction data, JCPDS – International Centre for Diffraction Date, 38-1420

# Index

<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC</td>
<td>Alternating Current</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic Force Microscope</td>
</tr>
<tr>
<td>APM</td>
<td>Ammonium Hydroxide Peroxide Mixture</td>
</tr>
<tr>
<td>BHF</td>
<td>Buffered HF</td>
</tr>
<tr>
<td>CMOS</td>
<td>Complementary Metal Oxide System</td>
</tr>
<tr>
<td>CNC</td>
<td>Computer Numerical Control</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical Vapor Deposition</td>
</tr>
<tr>
<td>CW</td>
<td>Continuous Wave</td>
</tr>
<tr>
<td>DC</td>
<td>Direct Current</td>
</tr>
<tr>
<td>DLC</td>
<td>Diamond-Like-Carbon</td>
</tr>
<tr>
<td>DUV</td>
<td>Deep Ultraviolet</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy Dispersive Spectrometry</td>
</tr>
<tr>
<td>EUV</td>
<td>Extreme Ultraviolet</td>
</tr>
<tr>
<td>FADS</td>
<td>Filtered Arc Deposition System</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full Width at Half Maximum</td>
</tr>
<tr>
<td>HAZ</td>
<td>Heat-affected-zone</td>
</tr>
<tr>
<td>IC</td>
<td>Integrated Circuit</td>
</tr>
<tr>
<td>IR</td>
<td>Infrared (Electromagnetic Radiation)</td>
</tr>
<tr>
<td>LIGA</td>
<td>Lithography – Electroforming – Molding (English Translation)</td>
</tr>
<tr>
<td>LPCVD</td>
<td>Low pressure CVD</td>
</tr>
<tr>
<td>LSCM</td>
<td>Laser Scanning Confocal Microscopy</td>
</tr>
<tr>
<td>MEMS</td>
<td>MicroElectroMechanical Systems (U.S. nomenclature)</td>
</tr>
<tr>
<td>MOS</td>
<td>Metal Oxide System</td>
</tr>
<tr>
<td>MST</td>
<td>Microsystems Technology (European nomenclature)</td>
</tr>
<tr>
<td>NA</td>
<td>Numerical Aperture</td>
</tr>
<tr>
<td>NASICON</td>
<td>Na Super Ionic Conductor; Na&lt;sub&gt;1+x&lt;/sub&gt;Zr&lt;sub&gt;2&lt;/sub&gt;Si&lt;sub&gt;x&lt;/sub&gt;P&lt;sub&gt;3-x&lt;/sub&gt;O&lt;sub&gt;12&lt;/sub&gt;, 0&lt;x&lt;3</td>
</tr>
<tr>
<td>PECVD</td>
<td>Plasma Enhanced Chemical Vapor Deposition</td>
</tr>
<tr>
<td>PLD</td>
<td>Pulsed Laser Deposition</td>
</tr>
<tr>
<td>PRF</td>
<td>Pulse Repetition Frequency</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>--------------------------------------------------</td>
</tr>
<tr>
<td>PSG</td>
<td>Phosphosilicate Glass</td>
</tr>
<tr>
<td>PVD</td>
<td>Physical Vapor Deposition</td>
</tr>
<tr>
<td>RBS</td>
<td>Rutherford Backscatter Spectroscopy</td>
</tr>
<tr>
<td>RF</td>
<td>Radio Frequency</td>
</tr>
<tr>
<td>RIE</td>
<td>Reactive Ion Etching</td>
</tr>
<tr>
<td>SC-1</td>
<td>Standard Clean 1</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SIMS</td>
<td>Secondary Ion Mass Spectrometry</td>
</tr>
<tr>
<td>SMA</td>
<td>Shape Memory Alloy</td>
</tr>
<tr>
<td>TCE</td>
<td>Thermal Coefficient of Expansion</td>
</tr>
<tr>
<td>TMAH</td>
<td>Tetramethyl Ammonium Hydroxide</td>
</tr>
<tr>
<td>UV</td>
<td>Ultraviolet (Electromagnetic Radiation)</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
</tbody>
</table>
Publications

Journal Publication


Conference Presentations


