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Low energy metal ion implantation of poly-di-methylsiloxane (PDMS) for increased biocompatibility for use in tissue engineering applications

Brad R. Winton

University of Wollongong

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Low energy metal ion implantation of Poly-di-methylsiloxane (PDMS) for increased biocompatibility for use in tissue engineering applications

A thesis in fulfilment of the requirements

for the award of the degree

DOCTOR of PHILOSPHY

from the

UNIVERSITY OF WOLLONGONG

By

Brad R Winton, MSci Hons, BSci Hons
Institute for Superconducting and Electronic Materials (ISEM)

August, 2010
Declaration

This is to certify that the work presented in this thesis was carried out by the candidate in the laboratories of the Institute for Superconducting and Electronic Materials at the University of Wollongong, NSW, Australia, and also The Australian Nuclear and Science Organization and has not been submitted for a degree to any other institution for higher education.

Brad R Winton
July, 2010
With endless gratitude for the endless support and encouragement from my supervisors - Mihail Ionescu and Shi Xue Dou - friends, family and colleagues.
Published and Presented Works as a Result of this Project


Scope and Motivation

The primary purpose of this work was the selection of a material for suitability as a non-biodegradable scaffold or support for use in the creation of artificial and semi-artificial soft tissue organs. With consideration of the literature review and the stated design considerations for tissue engineering, a polymer biomaterial, polydimethylsiloxane (PDMS), was selected for the research in this thesis. The appropriateness of polydimethylsiloxane for this application is further enhanced through the treatment and subsequent modification of the surface with low energy metal ion implantation. This treatment and modification adds further functionality to this already widely used biomaterial through the production and control of complex micrometer-scale topographical patterns on the surface and also the selective enhancement of the bioactivity of the surface through the introduction of complex polar functional groups to the surface.

The ease with which dominant and complex patterns can be generated and controlled on the surface of an elastomer film makes self-organising buckling an easy ‘bottom up’ way of creating and tuning different topographical structures on the submicron to micrometer scales for such applications as the creation of scaffolds and the spatial organisation of cellular cultures. This potentially provides a simple and inexpensive technique for rapid and reproducible cell patterning of substrates for tissue engineering, without the need for any pretreatment of the elastomer such as stretching or coating. Changes to the surface composition also provide a unique way to further optimise the surface properties of the polymer.

It is important that the self-organised, coherent, and semi-coherent 3D surface features be selectively induced onto the surface of the elastomer film. In this work, we have conducted a parameter study of this combined method of buckling, to understand the influence of various metal ion species, the varying geometric confinement of buckled areas onto a larger unmodified elastomer film, and the
boundary conditions of the said geometric confinement on the induced buckling regimes, thereby creating a simple non-photolithographic means of patterning soft materials.

Since this work has used optically active and magnetic ions in generating the topological surface changes, it is expected that at high doses the surface features become functionalised. A variety of metal ions were used, including Ni, Co, Fe, Au, Ti, Ta, Mg, and Eu, as well as combinations of them. The magnetic properties of Ni, Co, and Fe, and the optical properties of Eu are widely understood, and this method of producing buckling results in functionalised 3D surface structures with high elemental concentrations at the surface. So, this study also acts to demonstrate the creation and elemental functionalisation of 3D regular, self-organised, surface features via buckling in PDMS via metal ion implantation.

It will be shown that, as well as low energy metal implantation being an easy, one-step bottom up method for the creation and manipulation of complex micrometer-scale topographical surface relief patterns, the technique also serves as a relatively simple method of producing selected regions of biocompatibility, with all treated regions enjoying an increase in attached viable cells of over 450%, and with the Fe implanted surface showing a 600% increase. This enhancement in biocompatibility is achieved without altering the mechanical bulk properties and while retaining the negligible toxicity of the chosen polymer, PDMS.

Beyond the selection of a material for suitability as a non-biodegradable scaffold or support and the demonstration of the creation and control of 3D relief patterns, as well as the displayed increase in biocompatibility of the surface, a potential direction to take this research has been suggested through the establishment of a planar multi-electrode array (pMEA) system. Polysiloxane film is used as an insulating layer sitting between indium tin oxide (ITO) tracks embedded into the glass electrophysiology substrate. This work allows the potential of adding a further
method of control and manipulation of a cellular culture, which is electrophysiologically monitored through the modification of this elastomer layer.
Abstract

Poly-di-methylsiloxane (PDMS) thick films approximately 4 µm in thickness were spin coated onto a silicon wafer support in preparation for topological and chemical surface modification. Thorough mixing and time within a vacuum chamber ensured a bubble and defect free, homogeneous, quality PDMS elastomer film.

From these pristine quality PDMS thick films, films with three-dimensional features self-organized into coherent and semi-coherent buckling domains were then created by implanting different species of metal ions and combinations thereof, using a metal evaporation ion source, into these quality polydimethylsiloxane films. As a result of the implantation process, functionalized discrete regions of strain-induced surface buckling were created, taking the forms of domains of parallel surface waves, semi-ordered regions, and disordered regions. In addition, deep, strain-induced, V-shaped cracks were observed to penetrate well into the elastomer matrix. Furthermore, it was found that controlling the localized strain by altering the metal ion species could control the frequency of the V-shaped cracks and the properties of the buckled areas.

Thus, low energy metal ion implantation has been used to combine an easy ‘bottom up’ way of creating and tuning different topographic structures on submicron to micrometer scales with the embedding of a metallic element-rich functionalised layer at the surface for a variety of scientific and technological applications. The self-organising and complex patterns of functionalised topographic structures created through strain induced buckling are highly dependent on the implanted metal ion species, variations in the geometric confinement of the buckled areas onto the larger unmodified elastomer film, and the boundary conditions of the buckled regions. Characterization and systematic investigations of the strain induced buckling and its dependencies on geometric confinement, metal ion species, and its boundary conditions have been thoroughly investigated along with
possible mechanisms for the formation of the cracks and complex buckling domains.

Once it has been demonstrated that low energy metal ion implantation of PDMS films simultaneously allow for the creation of complex and tuneable surface topographical features, the surface modification effects of enhancing the biocompatibility of the surface for biological applications are investigated. PDMS thick films were implanted with Mg, Ta, and Fe at constant dose, and cellular cultures were used to test the surface modification effects on biocompatibility, along with any variation as a result of metal ion species. Cells cultured on all of the modified surfaces enjoyed an increase in viable cell count of over 450% when compared to the pristine surface, with the Fe implanted surface showing a 600% increase combined with a substantial increase in surface energy, which was reflected by the increased contact angle. This was achieved without any biochemical patterning requiring multiple processing steps, complex chemistries, or clean room facilities. The rapid prototyping and ease of creation makes this technique useful for the fabrication of selective and functionalised substrates and scaffolds for in depth bioanalytic studies, implants, and device components. The results of surface energy investigations, cross-sectional transmission electron microscopy, and compositional analysis, as well as initial biocompatibility testing are presented.

A planar micro-electrode array (pMEA) system has been set up as a potential direction in which this research work could be taken. In the planar multi-electrode array (pMEA) system, Indium Tin Oxide (ITO) conductors are covered by 3 μm of polysiloxane resin before the 64 electrodes at the centre of the plate are de-insulated and gold plated for reduced impedance. This elastomer coating is used both as an insulating material to minimise neuronal crosstalk and as a patterning material to guide growth of neuronal networks only to areas where there are electrodes present that are available for bidirectional communication. SH-SY5Y neuroblastoma cells have been cultured in a flask, trypsinised, and allowed to settle and adhere onto the electrophysiologically active glass slide. The bio-electrical spike
trains resulting from the live cell culture were recorded by the pMEA system and are presented in preparation for the potential continuation of this work.
Table of Contents

Low energy metal ion implantation of Poly-di-methylsiloxane (PDMS) for increased biocompatibility for use in tissue engineering applications................................................................. 1
Published and Presented Works as a Result of this Project ........... 4
Scope and Motivation................................................................. 5
Abstract ..................................................................................... 8
Table of Contents ....................................................................... 11
List of Figures: ............................................................................. 15
List of Tables................................................................................ 22
List of Abbreviations: ................................................................. 23
Part 1: Theory............................................................................ 24
  Chapter I: Introduction ............................................................. 24
    1.1 Biomaterials ...................................................................... 26
      1.1.1 Definition and Historical Development ................... 26
      1.1.2 Classes of Biomaterials .............................................. 29
        1.1.2.1 Metallic Biomaterials .......................................... 30
          1.1.2.1.1 Advantages and Applications ...................... 30
          1.1.2.1.2 Disadvantages ............................................ 30
        1.1.2.2 Ceramic Biomaterials ......................................... 32
          1.1.2.2.1 Advantages and Applications ...................... 32
          1.1.2.2.2 Disadvantages ............................................ 33
        1.1.2.3 Composite Biomaterials ..................................... 34
          1.1.2.3.1 Advantages and Applications ...................... 34
          1.1.2.3.2 Disadvantages ............................................ 35
        1.1.2.4 Polymeric Biomaterials ...................................... 35
          1.1.2.4.1 Advantages and Applications ...................... 38
          1.1.2.4.2 Poly-dimethysiloxane as a Biomaterial ......... 39
    1.2 Material Surface and Biological System Interfacial Interactions.................................................................................. 42
      1.2.1 Surface Modification of Biomaterials for Increased Biocompatibility ......................................................... 43
        1.2.1.1 Morphological Surface Modifications of Biomaterials For Increased Biocompatibility ............................... 44
1.2.1.2 Chemical Surface Modifications Of Polymeric Biomaterials For Increased Biocompatibility ............... 46
  1.2.1.2.1 Wet Chemistry Methods for Surface Modification ................................................................. 46
  1.2.1.2.2 Ionised Gas Treatments ............................................. 46
    1.2.1.2.2.1 Plasma .............................................................. 47
    1.2.1.2.2.2 Corona Discharge ........................................... 48
    1.2.1.2.2.3 Flame Treatment ............................................ 48
    1.2.1.2.2.4 UV Irradiation .............................................. 48
    1.2.1.2.2.5 Ion Implantation ........................................... 49
  1.2.1.3 Biochemical Surface Modifications Of Biomaterials For Increased Biocompatibility ......................... 50
1.3 Polysiloxanes ........................................................................ 51
  1.3.1 Introduction to the Field of Organosilicon Chemistry ... 51
  1.3.2 Preparation of polysiloxanes ......................................... 53
  1.3.3 Structural Properties of Linear Polysiloxanes .............. 53
  1.3.4 Thermal Stability and Degradation Behaviour Of Linear Polysiloxanes In a Vacuum or an Inert Environment ...... 54
  1.3.5 Thermo-Oxidative Stability and Degradation Behaviour Of Linear Polysiloxanes .......................... 57
1.4 Ion Implantation of Poly-di-methylsiloxane (PDMS) ........ 58
  1.4.1 Theory of Ion Polymer Interactions: a Physical Investigation .......................................................... 58
  1.4.2 Ion Implantation of PDMS: a Chemical Investigation ... 63
  1.4.3 Classical Theory of Buckling ........................................ 64
  1.4.4 Buckling in PDMS ...................................................... 67
Part 2: Experimental........................................................................ 70
Chapter 2: Material Preparation, Modification and Characterisation .......................................................... 70
  2.1 PDMS Processing .............................................................. 70
    2.1.1 PDMS Mixing and Degassing ....................................... 70
    2.1.2 PDMS Membranes: Spin Coating and Curing .............. 71
  2.2 Metal Ion Implantation (MEVVA) ..................................... 74
    2.2.1 Operation of Equipment and Production of Samples.... 76
  2.3 Surface Characterisation Techniques .............................. 78
    2.3.1 Microscopic Surface Characterisation Techniques .... 78
      2.3.1.1 Transmission electron microscopy (TEM) ......... 78
2.3.1.2 Scanning Electron Microscopy (SEM) ........................................ 80
  2.3.1.2.1 Field Emission Scanning Electron Microscope (FESEM) ............................................................... 82
2.3.1.3 Atomic Force Microscopy (AFM) ........................................... 84
2.3.2 Spectroscopic Surface Characterisation Techniques .......... 86
  2.3.2.1 Rutherford Backscattering Spectrometry (RBS) .............. 86
  2.3.2.2 Elastic Recoil Detection Analysis (ERDA) ..................... 88
  2.3.2.3 X-ray photoelectron spectroscopy (XPS) ...................... 90
  2.3.2.4 RAMAN Spectroscopy ................................................. 93
  2.3.2.5 Ultraviolet-Visible Spectroscopy (UV-Vis) .................... 94
2.3.3 Other Surface Characterisation Techniques ....................... 96
  2.3.3.1 X-ray Diffraction (XRD) ............................................. 96
  2.3.3.3 Contact Angle ............................................................ 98
  2.3.3.4 Biocompatibility Testing – Neuroblastoma Cell Culture ................................................................. 99
Part 3: Results and Discussion .......................................................... 101
  Chapter 3: An investigation of the pristine, unmodified PDMS thick film ................................................................. 101
  Chapter 4: Low Energy Metal Ion Implantation into PDMS .... 109
    4.1 Physical Consequences of Metal Ion Implantation of PDMS Thick Films: Investigation of the Onset and Evolution of Buckling ............................................................................. 109
    4.2 Chemical Implications of Metal Ions Implanted Into Elastomer Thick Films ............................................................... 126
Chapter 5: Controlling the Topography and Morphological Regimes of Buckling on PDMS ......................................................... 144
  5.1 Controlling the Buckling Regimes through the Use of Dose Effects .................................................................................... 144
  5.2 Controlling the buckling regime through the use of masks ... 148
Part 6: Functional uses and applications for low-energy metal implanted PDMS surfaces ......................................................... 156
  6.1 Functional evaluation of buckled surfaces for biological applications .............................................................................. 156
  6.2 Possible example for use of buckled elastomer thick film - Multi-electrode Array Recording System ............................................. 167
    5.2.1 Experimental ..................................................................... 171
    5.2.1.1 MEA Preparation .......................................................... 174
5.2.2 Results and discussion ...................................................... 175
Part 6: Conclusion ............................................................................ 180
Appendix 1: Published works ........................................................... 182
  Structural and morphological modification of PDMS thick film surfaces by ion implantation with the formation of strain induced buckling domains ................................................................. 182
  Buckling Induced Patterns in Thin Confined Elastic Films by Ion Implantation .................................................................................. 198
  The Control of Time-Dependent Buckling Patterns in Thin Confined Elastomer Film ........................................................... 205
References ......................................................................................... 241
List of Figures:

Figure 1: Schematic of a linear polymer backbone structure.................36
Figure 2: Schematic of a branched polymer backbone structure.........37
Figure 3: Different interfacial biological system – material interactions at various length scales.................................................................42
Figure 4: General polysiloxane backbone structure for PDMS............55
Figure 5: Penetration of Ni ions (red) into PDMS. The ion track (Red) triggers cascading collisions other constituent atoms within the solid polymer, H (green), C (blue), O (magenta) and Si (light blue). ..........................................................................................................................61
Figure 6: Energy loss for 5.49 MeV alpha particles in air with characteristic Bragg peak..............................................................62
Figure 7: Schematic of a) unbuckled PDMS elastomer film on a rigid Si base b) buckling, wrinkling without interfacial delamination, constrained on a Si base, and c) buckle delamination, wrinkling with interfacial delamination, constrained on a Si base.............66
Figure 8: Schematic of the manufacturing process for the creation of featureless, homogeneous thick PDMS films..........................70
Figure 9: Cross-sectional SEM of the unmodified PDMS thick film on supporting Si wafer under different spinning conditions. A) 4000rpm for 60s b)8000 rpm for 120s.........................................................72
Figure 10: Chosen spin-coating program for the manufacture of homogeneous, optically transparent films of PDMS on Si wafers ready for metal ion implantation.............................................72
Figure 11: Schematic of a MEVVA source with a cathode - anode arc discharge, trigger for starting the arc, and three-grid extraction system. ................................................................................................75
Figure 12: FIB lift-out of a PDMS membrane for cross-sectional TEM..80
Figure 13: Schematic representation of the key parts and functions of an AFM .........................................................................................84
Figure 14: Schematic of RBS used in this work.....................................87
Figure 15: XPS spectrum of a PDMS thick film implanted with Au ions (20 min exposure).................................................................92
Figure 16: Schematic diagram of the change in vibrational energy states as a result of monochromatic light. ..................................................94
Figure 17: Possible electronic excitations of organic molecules. ........96
Figure 18: Schematic illustrating Bragg’s Law.......................................97
Figure 19: Schematic of contact angle calculations. ............................ 98
Figure 20: SEM image of the surface of a PDMS film prior to ion implantation. The square in the middle is a beam focussing contamination spot. ......................................................... 101
Figure 21: SIMNRA analysis of ERDA on an unmodified PDMS thick film on a silicon support wafer. .......................... 102
Figure 22: RBS spectrum of unmodified PDMS on a Si support wafer. The small Te contamination on the surface of the Si wafer appears to be from process contamination present on the purchased wafers................................................................. 104
Figure 23: Raman laser spot on metal ion implanted PDMS thin film. 105
Figure 24: Raman spectrum of unmodified PDMS on a silicon support wafer. ................................................................. 106
Figure 25: UV-VIS spectrum of unmodified PDMS thick film on Si support wafer compared to spectra after a variety of doses of Fe ion implantation................................................................. 107
Figure 26: Optical photographs of cracks on the surface of ion implanted PDMS films: (a) 20 min Ti implanted, (b) 20 min Ta implanted. ................................................................. 109
Figure 27: Typical AFM scan of a characteristic heat induced surface crack. Note the V shape, indicating a strain-induced feature..... 110
Figure 28: AFM images of small surface crack associated with 3 min Co exposure of PDMS thick film supported on a Si wafer: (a) top view, and (b) 3D projection......................................................... 111
Figure 29: (a) SEM image of Ni + Eu implanted PDMS thick film; (b) back-scattered SEM image of Ni + Eu implanted PDMS thick film. ....... 111
Figure 30: Sectional AFM scan of the characteristic sine-function-like ripples. Different metal ion species result in altered frequency and amplitude of buckles. ......................................................... 112
Figure 31: AFM scan demonstrating the change in buckling amplitude with dose. (a) 1 min Co ion implantation; (b) 3 min Co ion implantation of PDMS thick film on a supporting Si Wafer ......... 113
Figure 32: AFM scan of buckling from 10 s Fe ion implanted PDMS film (a) displaying the adhesive nature of the buckled film and the ready picking up of debris; (b) friction AFM of the same sample. ................................................................. 113
Figure 33: AFM scan of the interface between the unmodified film and the metal ion implanted film. The film was partially covered with a piece of Al foil. ................................................................. 114

Figure 34: Complex buckling pattern around a surface crack for 15 min Fe ion implanted PDMS film on a supporting Si Wafer. .......... 115

Figure 35: Complex buckling pattern around the intersection of several surface cracks for 15 min Ni ion implanted PDMS film on a supporting Si wafer ................................................................. 116

Figure 36: Complex buckling pattern around the intersection of two surface cracks for 15 min Ni ion implanted PDMS film on a supporting Si wafer ................................................................. 117

Figure 37: The evolution of buckling effect with dose: a) with 5 s of Fe implantation, b) 25 s of Fe implantation, c) 3 min of Fe implantation. White area outside buckling is the unmodified film. ................................................................. 117

Figure 38: Optical microscope images of Fe implanted PDMS film. After 3 s of exposure, buckling is beginning to be initiated from surface debris and edges ........................................................................ 118

Figure 39: Introduced hole defect in the PDMS film produced spiral buckling patterns in the above 10 min Ti implanted PDMS film on a supporting Si wafer ........................................................................ 119

Figure 40: Optical image of both ordered and disordered buckling on the surface of the ion implanted PDMS. Partial domain structures are clearly visible away from the surface cracks. Inset: Lower magnification image of the film, showing the transition between the covered non-modified area and the modified surface . ....... 120

Figure 41: Complex buckling pattern of 900 s Ni and 900 s Eu ion implanted PDMS film on a supporting Si Wafer ....................... 121

Figure 42: Complex buckling pattern of 15 min Ni and 15 min Fe ion implanted PDMS film on a supporting Si wafer. Wear is evident in the bottom left from prolonged handling .................................................. 122

Figure 43: AFM of surface buckling for 180 s Fe implanted PDMS film ................................................................................................... 123

Figure 44: AFM across the intersection of strain induced buckling patterns: a) optical microscope image showing the region of interest, b) AFM scan across an intersection of strain wave fronts, in this case the corner of a polygon. This result is repeated across all intersections, and there is no evidence of delamination occurring. ........................................................................ 124
Figure 45: Incoherent buckling pattern of 20 min Au implanted PDMS film on a supporting Si wafer.

Figure 46: Multiple intersecting stress buckling fronts resulting in the appearance of a complex, multiple height bucking pattern in the above 10 min Ti implanted PDMS film on a supporting Si wafer.

Figure 47: Accelerated ion ranges for 45 keV Ni into a PDMS thick film calculated by SRIM: (a) Q = +1, 45 keV, (b) Q = +2, 90 keV, (c) Q = +3, 135 keV.

Figure 48: Collision cascade as a result of 45 keV Ni ions implanted into a PDMS thick film calculated by SRIM: (a) Q = +1, 45 keV, (b) Q = +2, 90 keV, (c) Q = +3, 135 keV.

Figure 49: RBS spectra of 45 keV Co implantation into a PDMS thick film with exposure of a) 60 s, b) 120 s, c) 180 s, d) 900 s.

Figure 50: RBS spectra of 45 keV Fe implantation into a PDMS thick film for a) 60 s, b) 120 s, c) 180 s, d) 900 s.

Figure 51: RBS spectrum showing results of Co implantation of PDMS film for 900 s followed by Eu implantation for 900 s.

Figure 52: Grazing angle XRD of Ni implanted PDMS thick film with exposure of 15 min (~17,000 shots). The increasing angle of incidence shows the strain induced peak shifts.

Figure 53: Grazing angle XRD of Ni and Fe implanted PDMS thick film, with implantation carried out for 15 min (~17,000 shots) for each ion species. The increasing angle of incidence shows the strain induced peak shifts.

Figure 54: Grazing angle XRD of Ni and Eu implanted PDMS thick film, with implantation carried out for 15 min (~17,000 shots) for each ion species. The increasing angle of incidence shows the strain induced peak shifts.

Figure 55: Grazing angle XRD of Si implanted PDMS thick film, with implantation carried out for 15 min (~17,000 shots) for each ion species. The increasing angle of incidence shows the strain induced peak shifts.

Figure 56: Grazing angle XRD of Co implanted PDMS thick film, with implantation carried out for 15 min (~17,000 shots) for each ion species. The increasing angle of incidence shows the strain induced peak shifts.

Figure 57: High resolution SEM image of surface porosity of the decomposed PDMS layer after ion implantation.
Figure 58: Cross-sectional TEM conducted on a focused ion beam (FIB) lift-out from the iron implanted PDMS sample: a) pristine cross-section; b) EDS contamination spots indicate the regions where EDS was conducted from the surface into the bulk. 

Figure 59: Cross-sectional TEM images of PDMS irradiated with Ni, Fe, and Au for 20 min, using an accelerating voltage of 50 kV and a beam current of ~1 mA. The black region is a metal coating grown on the surface as part of the focused ion beam (FIB) lift out process.

Figure 60: Optical Images of PDMS irradiated with Au (left), Ni (middle), and Fe (right) with exposure to ions for 20 min, using an accelerating voltage of 50 kV and a beam current of ~1 mA.

Figure 61: Evidence of increased ferromagnetic activity as a result of implanted metal rich layer. Since PPMS is a bulk technique and the metal rich layer is small, the ferromagnetic signals are also relatively small.

Figure 62: Dependence of wrinkle wavelength on the implanted metal ion. Ni, Ti, Eu, and Mg were also implanted at specific exposure times and found to follow the above sigmoidal trends.

Figure 63: RBS spectra of metal ion implanted PDMS films showing the presence of a metal rich volume within the polymer matrix.

Figure 64: RBS profiles of the metal layers in PDMS thick film for 1, 2, and 3 min exposure times. Note: the 3 minute exposure for Co is missing, since RBS showed a step rather than a peak.

Figure 65: Optical microscope images of the evolution of buckling in a circular island with increased dose of iron implantation. Exposure times are 5 s (a) and 30 s (b).

Figure 66: Au implanted PDMS thin film with 20 min of exposure in a 1 mm radius spot. The buckling wavelength at the edge of the spot is 3 μm larger than the wavelength at the centre of the spot.

Figure 67: Buckling pattern seen for a 5 s Fe ion implanted spot on a PDMS film. The effects of an inhomogeneous edge can be seen on the buckling initiation.

Figure 68: Semi-coherent buckling pattern as a result of 20 min Au implantation with a mask on a PDMS film on a supporting Si wafer.

Figure 69: Optical microscope images of the different buckling morphologies as strain increases: a) radial and hooping zigzag patterns from 5 s Fe implantation; b) telephone cord buckling from
20 min Fe implantation; c) random buckling fronts intersect, leading to a pattern of polygons bounded by telephone cord buckling in 20 min Fe implantation................................. 152

Figure 70: Optical microscope images of two different radius of curvature boundary conditions, for identical dose of Fe implantation, resulting in different strain buckling: a) large radius of curvature (island radius 5 mm) leading to three distinct regions of strain at the outside of the implanted island; b) small radius of curvature (island radius 1 mm) with lower strain, showing the beginning of the buckling edge effects; c) and d) AFM height profile results from across the edge of the larger and smaller metal ion implanted islands, respectively................................. 153

Figure 71: The edge of a large 20 min Fe ion implanted spot. The buckles within the spot can be seen to be bordered by nano-pillars, and then outside the spot, there are micro-buckling patterns an order of magnitude smaller than that seen within the spot away from the edge.............................................. 154

Figure 72: The edge of a large 20 min Mg ion implanted spot. The buckles within the spot can be seen to be bordered by nano-pillars, and then outside the spot there are micro-buckling patterns an order of magnitude smaller than that seen within the spot... 154

Figure 73: O/C and Si/C ratios for the surface of pristine and metal ion implanted PDMS................................................................. 158

Figure 74: Contact angle decreases with increasing exposure to energetic metal ions.............................................................. 159

Figure 75: Contact angle of native and modified PDMS in comparison with some other commonly used surfaces in cell culture work, glass and PMMA............................................................. 160

Figure 76: Surface energy increase with increased dose. This is consistent with an increase in surface polar groups as a result of pyrolytic decomposition. .......................................................... 161

Figure 77: Surface energy of native and modified PDMS in comparison with some other readily used surfaces in cell culture work, glass and PMMA.................................................................. 162

Figure 78: Optical microscope and corresponding fluorescence images of L929 cells after two days of culture on a) pristine PDMS, b) Mg implanted PDMS, c) Ta implanted PDMS, and d) Fe implanted PDMS. e) Mean data values of viable cell counts on each of the surfaces................................................................. 163
Figure 79: 3-D (A) and 2-D (B) cell cultures. ........................................ 169

Figure 80: (a) Base plate with heating resistors and an aluminium chamber block fastened with thumbscrews. MEA is connected to board with zebra stripes. (b) Electronics and base plate placed into a cast aluminium box with small hole cut out above and below chamber for visibility. (c) SH-SY-5Y cells adhered to a MEA with cell medium in a petri dish. Gasket is removed and the MEA is placed in the chamber block. (d) Cast aluminium box is placed onto a microscope stage with entire setup placed inside a Faraday Cage for the recording of bio-electrical signals from the cell culture. 172

Figure 81: 64 electrode MEA used in RAT system for the recording of evoked field potentials and spikes: (a) entire 5x5 cm glass plate displaying ITO tracks; (b) ~1mm recording area showing the 64 electrodes .................................................................................................................. 173

Figure 82: RAT Software acquisition: a) screen capture of RAT software live recording aligned to a 64 channel map (b), whereby individual spikes can be analysed (c). .......................................................................................... 174

Figure 83: Cell density too high, resulting in significant cell clumping. 176

Figure 84: Monolayer of SH-5YSY cells seeded on a 64-planar multi-electrode array (pMEA) with limited cell clumping. .................... 177

Figure 85: 4 representative electrodes showing the continuous background noise component. ......................................................... 178

Figure 86: Selected spike activity captured from the RATS software. 179
List of Tables

Table 1: Summary of different classes of bio-materials along with advantages, disadvantages, and common applications .............. 41
Table 2: Recently reported PDMS curing conditions. ......................... 73
Table 3: Sputtering Charge Probability (%)\textsuperscript{248}. ......................... 77
Table 4: Ion penetration ranges of different ionisation charge states in PDMS (nm). ................................................................. 77
Table 5: List of samples created, with ion elemental species used and times of exposure in seconds. All ion implanting was done on an approx. 4µm thick PDMS film on a supporting Si wafer. .............. 78
Table 6: Variational spectra of the PDMS (cured at 80ºC, mix 1:20) thick film. ................................................................. 106
Table 7: SIMNRA simulation of the atomic composition of PDMS with depth due to Co ion implantation................................. 129
Table 8: SIMNRA simulation of the atomic composition of Co and Eu ion implanted PDMS film. Each Ion was implanted for 900 s. ...... 131
Table 9: SIMNRA simulation of the atomic composition of PDMS with depth due to Co ion implantation................................. 132
Table 10: Location of and shift in broad PDMS peak from grazing angle XRD as a result of surface strain. ................................. 136
Table 11: Cross-sectional EDS results on iron implanted PDMS sample. Regions are indicated in Figure 31................................. 139
Table 12: XPS atomic composition analysis of native PDMS and metal ion implanted PDMS................................. 157
List of Abbreviations:

AFM: Atomic Force Microscopy
ECM: Extra-Cellular Matrix
ERDA: Elastic Recoil Detection Analysis
FESEM: Field Emission Scanning Electron Microscopy
LET: Linear Energy Transfer
MEVVA: Metal Vapour Vacuum Arc
ML: Molecular Layer
PDMS: Polydimethylsiloxane
PE: Polyethylene
PET: Polyethylene Terephthalate
PLA: Polylactic Acid
PMMA: Poly - Methyl Methacrylate
PP: Polypropylene
PS: Polystyrene
PTFE: Polytetrafluoroethylene
RBS: Rutherford Backscattered Spectrometry
SEM: Scanning Electron Microscopy
TEM: Transmission Electron Microscopy
UHPE: Ultra-High Molecular Weight Polyethylene
UV-VIS: Ultraviolet-Visible Spectroscopy
XPS: X-ray Photoelectron Spectroscopy
XRD: X-ray Diffraction
Part 1: Theory

Chapter I: Introduction

In 1988 at a National Science Foundation workshop, the term “tissue engineering” was coined to describe "the application and methods of engineering and life sciences toward fundamental understanding of structure-function relationships in normal and pathological mammalian tissues, and the development of biological substitutes to restore, maintain or improve tissue function\(^1\). Although some initial and scattered research was done in areas that lay within this definition, the modern and systematic field of tissue engineering has stemmed from the increased interest in artificial organs. Artificial organs in this context refer to artificial or semi-artificial devices or systems that permanently or temporarily perform the physiological functions of living tissue or organs in an attempt to solve the issue of the huge shortage of available tissues and organs available for transplantation. The current result of this shortage is a large number of people dying on waiting lists. The successful creation of artificial organs offers the potential for a new way of treating trauma, disease, and age-related loss of tissue function.

There are three main approaches to the creation of artificial and semi-artificial organs, the first of which is the creation of artificial tissue in-vitro through the use of isolated cells and biomaterials. Here, living cells are seeded into a precisely manufactured supporting matrix or scaffold of precise composition and structure such that cells can grow onto or into the implant or device prior to use or transplantation. This is exemplified by the work of Vacanti et al.\(^2, 3, 4\).

The second approach is the implantation of a cell-free biomaterial scaffold to guide the generation of new tissue. One of the earliest examples of this approach is Yannas et al.\(^5\), where fibroblasts were seeded into a sponge-like scaffold. The scaffold then acted like a dermal extracellular layer, with the aim being to control
the repopulation of the fibroblasts to minimize wound contraction and scarring. Finally, a cellular construct or device can be manufactured to generate functional tissues in-vitro for direct implantation or transplantation of cells\textsuperscript{6, 7}.

It should by this stage be self evident that all of these approaches to the creation of artificial organs through tissue engineering rely on the careful selection of the biomaterial from which the various systems or devices are made. This selection provides a scientist with a critical design consideration, because the selection depends upon the specific use or requirements, regardless of whether the biomaterial is used as an implanted cellular construct, or an acellular scaffold, or a component in a larger physiologically active device. Materials should be considered as not just a static replacement, but also as a way to harness cellular interactions and to manipulate cellular responses.

Several mechanical and biological design considerations when selecting a biomaterial become important, including:

1. The degree of support for new tissue growth, including maximising the access to nutrients, growth factors, and other pharmaceutically active agents;
2. The selectivity of cellular adhesion or activation on the surface or scaffold, including both enhancement and inhibition of adhesion and biocompatibility;
3. The ease in obtaining and manufacturing the final product;
4. The mechanical properties of the biomaterial both short-term and long-term, and an assurance of its long term functionality; and
5. The low or negligible toxicity of any degradation products of the biomaterial when placed in contact with a physiologically active system.

Two decades on, although the control and regulation of natural tissue regeneration for defect repair or even organ regeneration is still some way off, research into the
area of artificial organs has generated great progress, including the engineering of cartilage tissue, myocardial tissue engineering, liver tissue equivalents, and the guidance and regeneration of spinal tissue using polymer scaffolds.

1.1 Biomaterials

1.1.1 Definition and Historical Development

The definition of a biomaterial has been selected to neatly dovetail into the above definition of tissue engineering. As such, in the context of this work, it has been defined as ‘a material intended to interface with biological systems to evaluate, treat, augment, or replace any tissue, organ, or function of the body’. Today, using this broad definition encompasses a dizzying array of biological and medical applications and technologies, such as drug and gene delivery systems, tissue engineering, cell therapies, organ printing and cell patterning, nanotechnology-based imaging and diagnostic systems, and microelectronic devices that utilise an equally broad array of materials such as metals, ceramics, and synthetic polymers, but also biopolymers, self-assembled systems, nanoparticles, carbon nanotubes, and quantum dots. However, this work is only concerned with biomaterials immediately relevant to tissue engineering.

Although it would seem simple to design a material to interface with physiological systems, due to the complexity and dynamics of biological systems interacting with material surfaces, the field of biomaterials requires contribution both from fundamental disciplines, such as biology, physics, and chemistry, and from applied sciences, such as medicine and engineering. It is further complicated by the fact that the building and understanding of theoretical models is still at a relatively early stage and available only for very simplified cases. As an illustration, it should be noted that the first principles calculations for adsorption of the simplest amino acids onto ideally flat surfaces are just about to be achievable. With rapidly
developing fields and technologies outside of tissue engineering, such as bio-analytical technologies, DNA and protein microarrays, and bioinformatics, a more mechanistic understanding of biological processes and their causes should not be too far away.

This leaves most research in biomaterials science relying on empirical observations, phenomenological concepts and principles, know-how, and skills and experience, drawn from all the above listed disciplines, while another part is obtained particularly from research and investigation into the biomaterials. There is, however, no question that the field has come a very long way since dental implants were created with pieces of shell, wood and wrought-iron from periods as early as 100 AD.

It is probably recognised that the modern field of biomaterials, at least from a polymeric bias, started in the 1940s, when Harold Ridley noticed, from his examination of Spitfire fighter pilots who had shards of plastic, usually perspex, canopy unintentionally implanted in their eyes from enemy machine gun fire, that these shards seemed to heal with minimal long term effects and only minimal amounts of inflammation. He concluded that the canopy plastic, Poly - Methyl Methacrylate (PMMA), might be suitable for implant lenses to replace natural lenses with cataracts. The 1940s also coincided with a better appreciation of biocompatibility and sterilisation techniques, which ensured greater success when using biomaterials for scientific, technical, or medical applications.

From there, Harold Ridley in the 1950s, then an employee of St. Thomas’ Hospital, implanted the first intraocular lens (IOL). This lens was a clear, polymeric lens that was surgically inserted into the patient’s eyes after the removal of the natural lenses. The first Ridley lenses made of PMMA were placed just behind the iris and in front of the posterior capsule. Inevitably for such groundbreaking work, there were complications in approximately 15% of the patients following the implantation of these lenses. This led to the removal of the implanted lenses due to complications
including uveitis, secondary glaucoma, hyphaemia, decentration, and dislocation. Although the first generation lenses were relatively successful, they left much room for improvement, and today, his observations and innovation have led to the development of the modern intraocular lens (IOL), which is implanted in over 10 million eyes each year.

At around this time, pioneers were proving feasibility, saving lives, and laying the foundations which scientists are building upon today. Sir John Charnley was developing the hip implant which was first used in 1969, Vorhees was inventing the vascular graft\textsuperscript{15}, Willem Kolff was revolutionizing kidney dialysis, and Dr. Charles Hufnagel was inventing the ball and cage heart valve.

By the late 1960s, there existed a large degree of collaboration between chemists, biologists, and physicists to formulate design strategies and synthetic strategies for biomaterials. The toxicology, or the idea that toxins could leach from biomaterials, which would adversely affect healing, was formalized and now forms the basis for the modern idea of biocompatibility.

Scientists around this period started to move away from the early view that biocompatibility defines a material that is fully accepted into the body and not treated as foreign. Any artificial construct, no matter the degree of chemical inertness, will always cause contact-induced reactivity in the biological environment in the form of foreign body reaction, because it does not behave like natural tissue. Bone, for instance, is both stiff and elastic; it degrades and rebuilds itself, constantly adapting to changes. Metals and ceramics lack these properties. Yet each year over half a million total hip and knee arthroplasties occur in the US alone\textsuperscript{16, 17, 18}, and many more worldwide. Through surface contact with implants, the body attempts to coat, degrade, or encapsulate the material to varying degrees\textsuperscript{19}, leading to a second operation in over 14% of these cases. There is also a 0.5-5% risk of infection due to the region of immune depression that occurs in the interstitial locale surrounding the artificial implant\textsuperscript{20}, arising from damage during
surgery, or the micro-movements of the implant against hard tissue and the detrimental release of wear debris, which can cause additional complications.

New ideas and developments in biology and materials science were quickly incorporated into biomaterial studies, and molecular biology opened up and continues to open up new frontiers into biomaterial design. In particular, wide recognition among scientists that interfacial, chemical, and topological, rather than purely bulk, properties are the prime determinants in biocompatibility, have shifted the focus of research in biomaterials. When considering whether to use polymers, metals, ceramics, or composite materials as a non-biodegradable scaffold or support for use in the creation of artificial and semi-artificial soft tissue organs, a researcher must consider whether the bulk properties of the material are appropriate for the application they have in mind, as well as the material surface – biological system interface.

1.1.2 Classes of Biomaterials

Tissues are grouped into both hard and soft categories, with bone and teeth generally being categorised as hard tissues, while skin, blood vessels, cartilage, and ligaments are classified as soft tissues. In general, hard tissues have a greater elastic modulus and tensile strength than soft tissues. So, when considering the neat division of biomaterials into four broad classes, metallic, ceramic, composite, and polymeric, each class shows some advantages and disadvantages, which both limits their usefulness and guides them into specific applications, a summary of which can be found at the end of the chapter (Table 1). Ceramic and metallic biomaterials, with their higher elastic moduli, are frequently used for hard tissue applications, while polymers are primarily used for soft tissue applications. Even so, this can cause problems. Metals and ceramics have elastic moduli 10-20 times greater than for hard tissue, thereby creating stress shielding and leading to bone atrophy. Therefore, it is important to balance the advantages and disadvantages of each
class of biomaterial and reach the best compromise possible, and it is quite usual to use the three types of materials in the same implant or to use composite materials.

### 1.1.2.1 Metallic Biomaterials

#### 1.1.2.1.1 Advantages and Applications

The excellent mechanical properties, both in terms of strength and resistance to fracture, of metal biomaterials make them an excellent choice for load-bearing scientific and technological applications. Processing and heat treatments, including annealing, quenching, and aging, allow for the manipulation of the phase and morphology to better control the mechanical properties, without changing the chemical composition. This gives greater control over the manufacture of the devices and implants utilizing metals.

Metallic biomaterials are thus primarily used in applications that utilize their good load-bearing mechanical properties, such as orthopedics and dentistry, however, they can also be found in applications in cardiology, such as heart valves and vascular stents. Common metallic biomaterials include stainless steel, in the forms of austenite, martensite, and ferritic steels, due to their high hardness and corrosion resistance, cobalt alloys, which display greater corrosion resistance and greater wear resistance than stainless steels, and titanium and its alloys with its excellent biocompatibility and corrosion resistance, and its relatively low density. Like other classes of biomaterials, as new metals and alloys are manufactured, their roles in a growing and increasingly diverse field of applications are found.

#### 1.1.2.1.2 Disadvantages

However, despite the excellent mechanical properties of metallic biomaterials, the biocompatibility of metals range from only fair to good, depending upon the
corrosion resistance of the metal being used. The corrosion of metallic biomaterials and implants leads to the potential weakening of the device or implant and the toxic release of metallic ions through an oxidation/reduction reaction. Elements such as Ni, Cr, and Co are found to be released from stainless steel and cobalt chromium alloys due to the corrosion in the body environment\textsuperscript{21}. Wapner has reviewed the toxic effects of these elemental ions released from prosthetic implants\textsuperscript{22}. Skin related diseases such as dermatitis due to Ni toxicity have been reported, and numerous animal studies have shown carcinogenicity due to the presence of Co\textsuperscript{23}.

When metals are placed in contact with a physiological environment, an electrochemical reaction involving the dissolved oxygen and water molecules in aqueous body fluid, leading to their reduction to hydroxyl groups takes place. Oxygen depleted environments such as microcracks and crevices on the surface of the metallic biomaterial can acts as an anode to the rest of the metal surface, which behaves as a cathode due to electrons moving through the metal body to the higher oxygen content. This leads to either the use of noble metals due to their naturally inert properties or of metals which form passive films on the surface. This is the case, for example, with stainless steel forming a chromium oxide layer and titanium forming a titanium oxide layer.

The very same excellent mechanical strength that makes metallic biomaterials an excellent choice for load-bearing implants, when compared to that of normal tissue, make it a very poor choice for their use in tissue engineering scaffolding for soft tissues engineering applications. Because their density is vastly different from that of soft tissues, their use in tissue engineering involving soft tissues is almost non-existent. Even in hard tissue applications, there needs to be a modulus equivalency, as higher stiffness of bone implants than bone prevent the needed stress from being transferred to adjacent bone, resulting in bone resorption around the implant and consequently to implant loosening. This biomechanical incompatibility that leads to death of bone cells is called the “stress shielding effect”\textsuperscript{24}. 
Thus, for the scope of this work, which involves soft tissue engineering applications, metallic biomaterials have been disregarded.

1.1.2.2 Ceramic Biomaterials

1.1.2.2.1 Advantages and Applications

Ceramics, on the other hand, are used widely as artificial or semi-artificial organs due to their excellent biocompatibility with hard tissues, as well as soft tissues such as skin and muscle\textsuperscript{25, 26}. They are almost universally used in prosthetics and other biomedical applications where impact resistance is not an issue, and in tissue engineering as supporting scaffolds for tissue cultures and hard tissue formation, as well as carriers for bioactive molecule delivery, with hydroxyapatite and bioactive glasses being the most common.

Ceramic biomaterials can be broadly categorized depending upon their application and degree of interaction with the biological system, which ranges from inert to resorbable. The foreign body reaction kicks in when an inert or nearly inert material is implanted into the body, which leads to the implant being walled off by a layer of fibrous tissue. Porous implants, typically hydroxyapatite, provide a large interfacial area, which leads to bone growth into the pores, creating a strong mechanical bond. This prevents loosening of the implant, allowing for the withstanding of complex stress states. Bioactive implants, typically hydroxyapatite and bioactive glasses, quickly form a chemical bond with the interface of the implant. Resorbable implants are designed to degrade non-toxicially, being replaced over time by repaired natural tissue.

This neatly covers the three generations of bioceramics, where the first generation is primarily inert ceramics such as zirconia and alumina, which are commonly used
in the fabrication of femoral heads\textsuperscript{27}. Second generation bioceramics include bioactive and resorbable ceramics, such as bioactive glasses, calcium phosphate cements, and ordered mesoporous silica materials. Second generation bioceramics fulfilled the need to increase the bioactivity of first generation bioceramics while trying to reach mechanical properties similar to those of the hard tissue that they replace, such as natural bone. Third generation bioceramics aim to act as a scaffold and also to be porous. They are designed to act as a scaffold for cellular growth so that the cells can accomplish their regular function. This porosity, however, implies a certain sacrifice of their mechanical properties. They also require a certain degree of intelligent behaviour, so that they can modify their properties in response to certain stimuli. In addition, it is required in some cases to allow the loading of biologically active molecules onto such ceramics.

\textbf{1.1.2.2 Disadvantages}

Although they do not suffer from the risk of corrosion under exposure to physiological pH in biological systems, unlike metallic biomaterials, the use of ceramic biomaterials has traditionally been limited due to their mechanical properties such as their inherent brittleness, low tensile and impact strength, and susceptibility to micro-notches and cracks. However, unlike metal and alloy biomaterials, this mechanical weakness of bioceramics can be partially offset during manufacture. Nevertheless, it is these poor mechanical properties that limit their application to coatings, composites, and porous scaffolds in the field of tissue engineering.

The primary application for ceramic biomaterials, as discussed above, is their role in supporting scaffolds for tissue cultures and hard tissue formation. As such, they lie outside the scope of this work on tissue engineering of soft tissue.
1.1.2.3 Composite Biomaterials

1.1.2.3.1 Advantages and Applications

Composite materials are viewed as two or more distinct materials or phases on a scale larger than atomic. Composites allow a scientist or engineer to design and manufacture a material where control over material properties is important, such as in the creation of a stiff, strong, lightweight material that is also highly resilient. When designing and manufacturing such a composite, the separate materials or phases must all be biocompatible, and none capable of being degraded by the biological environment. While manufacturing a material that both mechanically and chemically is a perfect match for the scientific or technological application envisaged, the cost and difficulty of manufacture must be taken into account.

As a case in point, controlling the volume fractions, and the local and global arrangement of the reinforcing phase, allows for the tailoring of the mechanical and physiological compatibility of the composite to a biological system. Typical composites used in tissue engineering applications for the creation of artificial and semi-artificial organs are fiber-reinforced composites, especially polymer composites. Fiber reinforced polymer composites can include carbon fiber, Kevlar®, and glass fibers used to reinforce epoxy resin, polyetheretherketone (PEEK), polysulfone (PS), polysiloxanes, and others. By tailoring the type of polymer matrix and the type and amount of fiber reinforcement, both mechanical properties and the degree of biocompatibility can be controlled.

Advantages of developing and using polymer composite biomaterials include: the absence of corrosion and fatigue failure of metal and alloy biomaterials, the radio transparency of polymer composites, and the fact that they are fully compatible with modern diagnostic techniques.
The use of particulate fillers within polymeric biomaterials to create polymer composites is also common. The purpose is to tailor both the mechanical properties and the degree of biocompatibility. Such composites have been used successfully in clinical applications such as dental resins and bone cement. One key advantage of using particulate fillers over fibers to reinforce polymer matrices is that it has been shown that the addition of basic fillers can be used to control the biodegradation mechanism and rate. Examples include the addition of fillers such as hydroxyapatite and magnesium oxide to poly(L-lactide) and poly(DL-lactide) to change the degradation mechanism and rate.

1.1.2.2 Disadvantages

Despite the seemingly overwhelming advantages of composite materials over monolithic biomaterials such as polymers, metals, and ceramics, there are some key disadvantages. Manufacturing and designing composite materials reliably and with good reproducibility is often challenging and costly. Also, there can be problems with the long-term stability in a potentially aggressive biological system. The body's internal environment can have a pH ranging from 1-9, bones undergo stresses of up to 4 MPa, with ligaments and tendons undergoing peak stresses of 40-80 MPa, while these stresses repeat and fluctuate with activity. So, like the other classes of biomaterials, the advantages and disadvantages must be weighed and depend upon the application.

1.1.2.4 Polymeric Biomaterials

A polymer is a large molecule composed of repeating structural units, usually connected by covalent chemical bonds and having a wide range of physical and chemical properties. A key advantage of polymers over ceramics or metals for use as biomaterials is the ease with which its properties can be tailored for specific
technological and scientific applications, and the ease with which it can be fabricated into a variety of shapes.

The microstructure of the polymer, the physical arrangement of repeating units along the backbone of the chain, plays a key role in the tailoring of its macroscopic properties. Polymeric materials can fall into linear, branching, or cross-linked architectures.

The simplest architecture is a linear backbone structure, where there are no chemical bonds between polymer chains, so that when heated or placed under stress, these chains can move relative to each other. Ring architecture polymers are also classified as linear polymers.

![Figure 1: Schematic of a linear polymer backbone structure.](image)

A branched polymer molecule is composed of a main chain with one or more side chains or branches. Branching of polymer chains affects the ability of chains to slide past one another by altering intermolecular forces, and in turn, affecting bulk physical polymer properties. Long chain branches may increase polymer strength, toughness, and the glass transition temperature due to an increase in the number of entanglements per chain. Random length and atactic short chains, on the other hand, may reduce polymer strength due to disruption of organization and may likewise reduce the crystallinity of the polymer.
An effect related to branching is chemical cross-linking; this is where the polymer forms covalent bonds, creating a three-dimensional network. A gel is created where all the chains are linked to at least one molecule, leading to an almost infinite degree of cross-linking. Cross-linking tends to increase the glass temperature and increase strength and toughness, and with a few exceptions, cross-linking also ensures that the polymer cannot be dissolved in solvents when made molten through heating.

When discussing the microstructure of cross-linked polymers, the crystallinity of the polymer cannot be ignored. When applied to synthetic polymers, the term crystalline has been used in this work to describe regions of three-dimensional ordering on atomic (rather than macromolecular) length scales, arising from intramolecular folding and/or stacking of adjacent polymer chains. Synthetic polymers consist of both crystalline and amorphous regions, although polymers with microcrystalline regions are generally tougher and more impact-resistant than totally amorphous polymers\textsuperscript{31}. Polymers with a degree of crystallinity approaching zero or one will tend to be transparent, while polymers with intermediate degrees of crystallinity will tend to be opaque due to light scattering by crystalline or glassy regions. Thus for many polymers, reduced crystallinity may also be associated with increased transparency.
1.1.2.4.1 Advantages and Applications

The different polymers, both natural and synthetic, that chemists can manufacture number in the billions, each with its own chemical and mechanical properties. Polymers with similar chemical characteristics may even behave differently. Polyethylene and ultra-high molecular weight polyethylene (UHPE) behave differently as orthopedic implants, and UHPE shows lower wear and debris formation. This allows for greater selection and matching of polymer structural and mechanical properties for scientific and technological applications.

While polymers can be natural, such as proteins and polysaccharides, or synthetic, such as polyurethanes and organosilicones, biodegradable or non-biodegradable, synthetic polymeric materials have been widely used in medical disposable supplies, prosthetic materials, implants, dressings, drug delivery systems, and tissue engineered products, much like ceramics and metals. Unlike metal and ceramic biomaterials, however, polymeric biomaterials are easy and quick to manufacture in a variety of shapes at a reasonable cost, and it is relatively easy to conduct secondary processing. On the other hand, the mechanical and physical properties are not as good as those of either ceramics or metals.

While synthetic non-biodegradable polymers have found application as biomedical implant materials, as a substrate for micro-fluidic devices, for cell array fabrication, and for fundamental cellular studies, their usefulness in the field of tissue engineering or, more specifically, their usefulness in the creation of artificial and semi-artificial soft tissue organs is owed to their functional properties and design flexibility. Polymers are the primary choice of materials for making either naturally derived polymer or synthetic polymer scaffolds.
1.1.2.4.2 Poly-dimethysiloxane as a Biomaterial

Siloxane-based elastomers, such as polydimethylsiloxane (PDMS), have been heavily exploited in microtechnology, since they are homogeneous, isotropic, and optically transparent down to 300 nm. In its cross-linked state, the elastomer does not permanently deform under stress or strain, and it is stable over wide ranges of temperature and humidity. PDMS allows for quick and low cost fabrication by casting to form structures which feature sizes down to 100 nm, for example for moulds and stamps for nano-imprint lithography.

PDMS is very flexible, with a Young’s modulus $E = 1$ MPa, but its stiffness can be increased by a supporting layer such as a silicon wafer. It has a low interfacial free energy, which prevents most polymer molecules from reacting to or sticking to the surface, making it relatively chemically inert; the free energy can be tuned with irradiation. It is, however, relatively porous, with a strong tendency to adsorb specific molecules. This behaviour is disadvantageous in analytic devices, where it can lower separation efficiencies, but this disadvantage has been turned into an advantage in an alternative application in micro-contact printing (CP), in which a patterned PDMS stamp is used to adsorb alkanethiol inks. The inks are then transferred to a gold surface as a self-assembled monolayer, by binding of the terminating thiol (–SH) group to the Au.

These properties make PDMS attractive for use in a variety of scientific and technological applications that range from the production of active and passive medical implantation devices that are in direct and sometimes prolonged contact with human tissues, from artificial lungs to artificial finger joints, to technological applications such as microfluidics and lab-on-chip devices to building memory storage devices, stretchable electronics, optical diffraction gratings, optical microlenses and biosensors, and pharmaceutical applications, including porous PDMS membranes to control the release of drugs in dermal patches and tablet coatings.
It is the biocompatible material aspect of PDMS which makes it attractive as a biomedical implant material\textsuperscript{32}, as a substrate for microfluidic devices, and for cell array fabrication\textsuperscript{33} and fundamental cellular studies\textsuperscript{34} that is of most interest for this work. Unfortunately, despite its versatility, the low surface energy and hydrophobic nature of PDMS inhibit its bioactivity\textsuperscript{61}. This non-optimal biocompatibility has been addressed in the past through biochemical coatings\textsuperscript{62, 63} and physico-chemical treatments of the elastomer, including surface grafting\textsuperscript{64}, plasma discharge using various gases and excitation frequencies\textsuperscript{65, 66}, corona discharge\textsuperscript{67}, laser ablation\textsuperscript{68}, microwave irradiation\textsuperscript{69}, and ultraviolet (UV) modification\textsuperscript{70, 71}. This type of treatment has been widely used to improve the cellular adhesion on silicone surfaces by affecting the wettability of the elastomer surface\textsuperscript{72, 73}. 
Table 1: Summary of different classes of bio-materials along with advantages, disadvantages, and common applications

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<thead>
<tr>
<th>Materials</th>
<th>Advantages</th>
<th>Disadvantages</th>
<th>Applications</th>
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<tbody>
<tr>
<td><strong>Polymers:</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyethylene, Polyethylene</td>
<td>Low density and easy to fabricate. Flexible with tissue equivalent density.</td>
<td>Low mechanical strength and wear resistance. Wetting characteristics are</td>
<td>Cardiovascular, ELISA dish surface, soft skeletal tissue, dental implants,</td>
</tr>
<tr>
<td>Polytetrafluoroethylene</td>
<td></td>
<td>often not optimal. May degrade over time</td>
<td>bone cement, intraocular lens, catheters and tissue adhesive</td>
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<tr>
<td>Polystyrene, Polyurethane,</td>
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<tr>
<td>Silicone rubber</td>
<td>Resilient</td>
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<tr>
<td><strong>Metals and Alloys:</strong></td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Titanium, Stainless Steel,</td>
<td>High impact strength and wear resistance</td>
<td>Corrosion in the human body</td>
<td>Joint replacements Dental implants Bone Plates and Screws</td>
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<tr>
<td>Nickel</td>
<td></td>
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<tr>
<td>Titanium, Cobalt-chromium</td>
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<tr>
<td><strong>Ceramics:</strong></td>
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<tr>
<td>Alumina, Zirconia, Calcium</td>
<td>Good biocompatibility, corrosion resistance</td>
<td>Undesirable surface properties, weak in tension, and special techniques</td>
<td>Dental and Orthopedic Implants</td>
</tr>
<tr>
<td>Phosphates including hydroxyapatite</td>
<td></td>
<td>required for fabrication</td>
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</tr>
<tr>
<td><strong>Composite materials:</strong></td>
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<tr>
<td>Carbon-Carbon, wire or fibre</td>
<td>Designer physical or chemical properties. Possible by varying components</td>
<td>Difficult to make</td>
<td>Assist regeneration of natural tissue Bone cement</td>
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<td>reinforced bone cement</td>
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1.2 Material Surface and Biological System Interfacial Interactions

Since the chosen definition for biomaterials is 'a material intended to interface with biological systems to evaluate, treat, augment or replace any tissue, organ or function of the body', an understanding of the interaction between a material’s surface and a biological system is important for both the understanding and development of novel biomaterials, as well as for the improvement and optimisation of currently used biomaterials. When a biomaterial’s surface is exposed to a biological system, there are many interfacial and surface reactions occurring on different length scales, such as initial water adsorption, and subsequent adsorption of biomolecules such as proteins and later cell attachment to the material surface, as illustrated schematically in Figure 3.

Figure 3: Different interfacial biological system – material interactions at various length scales.
These reactions are determined by a number of factors, including chemical composition, surface energy, roughness, and topography of the top surface layers that are in contact with the biological system. Surfaces thus play an important role in a biomaterial’s effectiveness in both biology and medicine. Cellular adhesion to a biomaterial surface is a critical indicator of its effectiveness as a biomaterial, since cell adhesion occurs before other biological events, including cell spreading, cell migration and differentiation, and cell functions. Cell adhesion is closely related to the surface properties of biomaterials, including chemical structure, hydrophilicity and hydrophobicity, ionic groups, and surface morphology, including the domain structure of a multicomponent system, such as crystalline and amorphous domains, and the surface topography.

1.2.1 Surface Modification of Biomaterials for Increased Biocompatibility

The properties of a material rarely match perfectly every requirement for a given application, so it often becomes necessary to strike a compromise where a material has acceptable properties in each pertinent area. This inevitably leads to a focus not just on improvement and optimisation of current biomaterials, but also on the modification of surfaces of conventional materials that would not otherwise be useful as biomaterials.

Although bulk properties dictate the mechanical properties of biomaterials, tissue–biomaterial interactions depend on the surface of the biomaterial, which is in direct contact with living tissues in the body, and on the initial response of the living tissue to the biomaterial. Thus, initial interaction between the host and implant involves the conditioning of implants by serum and other tissue fluids, thereby resulting in compositional changes at the biomaterial surface. Thus, the tissue/cellular behaviour at the biomaterial–tissue interface must be improved.
This has led to a large focus on the area of surface modification. Surface modification is an effective approach to alter biological interactions of a particular material by only changing the outermost surface, without impacting upon the bulk properties of the material. This allows for a greater flexibility when designing and engineering solutions to technological and scientific applications, such as selective surface modification allowing for the spatial organization of cells, which plays a critical role in fundamental biological studies\textsuperscript{75}, as well as in the development of tissue engineering scaffolds\textsuperscript{76}, biosensors\textsuperscript{77,78}, and microfluidic assays \textsuperscript{79, 80}. Surface modification can provide accessible and chemically functional groups for the immobilization of drugs, enzymes, antibodies, or other biologically active species for a variety of biomedical applications, while high surface area geometries can enhance reaction turnover rates\textsuperscript{81}. Many surface modification techniques, morphological, chemical, and biological, have been used to produce various surface properties of polymers, often in sequence and as a precursor to tethering bioactive compounds to the surface. Tethering a bioactive compound to a solid substrate via a spacer molecule created through chemical modification of the surface can also improve bioactivity by reducing steric constraints and shielding the compound from hydrophobic surface induced denaturation.

**1.2.1.1 Morphological Surface Modifications of Biomaterials For Increased Biocompatibility**

Morphological modification refers to changing the surface roughness, by introducing grooves and other surface relief patterns, commonly through mechanical polishing, machining, grinding\textsuperscript{82, 83, 84}, sandblasting\textsuperscript{85}, casting\textsuperscript{86}, etching\textsuperscript{87}, electropolishing\textsuperscript{88, 89}, lithographic techniques, and deposition of rough or porous coatings\textsuperscript{90, 91, 92, 93}.

3D relief structures such as microgroove and ridged surfaces have been shown to offer significant control over cellular behaviours, including cell spreading, alignment, and migration along the grooves or ridges. Two main theories currently
exist to explain these phenomena: the first suggests that cell integrin receptors in local contact with cellular cultures transfer the variable degrees of tension or compression into the cytoskeleton, and cell stretch receptors subject to these stresses will be activated and reorganize the cytoskeleton according to the surface topography. This theory is called the contact guide effect. Another theory simply suggests that changes of surface free energy due to the edges and disruptions may be the reason for the cell orientation. It is well known also that cellular responses to the surface topographies are also influenced by the dimensions of the surface features, ranging from nano-, submicron-, to micro-scales, depending on the cell types and cell–cell interaction, as well as substrate composition and topography. Examples of this influence on cellular responses include the enhancement of the adhesion of a marine spore and the decrease in adhesion by endothelial cells when grown on rectangular ridges 5 µm wide and 1–5 µm high. Microgrooves of a variety of depths and widths on polylactic acid (PLA) or Polystyrene (PS) surfaces were found to enhance mineralized extracellular matrix (ECM) production and cell alkaline phosphatase activity of rat bone marrow cells over that of smooth surfaces, while micropillars 6 µm high with a variety of diameters on a PDMS surface were found to promote the spreading and adhesion of human bone marrow-derived connective tissue progenitor cells.

Good reviews and other studies exist that look at the correlation between surface topography and cell attachment and migration, with a number of recent works that are focused on micrometric topography, in such forms as grooves, ridges, pits, and islands.
1.2.1.2 Chemical Surface Modifications Of Polymeric Biomaterials For Increased Biocompatibility

1.2.1.2.1 Wet Chemistry Methods for Surface Modification

This classical method of surface modification involves a material being treated with liquid reagents to generate reactive functional groups on the surface. It is capable of penetrating porous three-dimensional substrates and allows for in-situ surface functionalisation of microfluidic devices. However, by their very nature, wet chemical methods are non-specific in producing a range of oxygen-containing functional groups and often depend on side chain surface orientation, limiting repeatability between polymers of different molecular weight, crystallinity, and tacticity. The production of hazardous chemical waste and irregular surface etching\textsuperscript{109} are also of primary concern, since many of these techniques also require extended treatment in concentrated corrosive solutions.

Some examples of this surface modification method include: chromic acid and potassium permanganate in sulfuric acid to introduce reactive oxygen-containing moieties to polyethylene (PE) and polypropylene (PP)\textsuperscript{110, 111, 112, 113, 114}; concentrated sodium hydroxide and sulphuric acid to generate carboxylic acid groups by base and acid hydrolysis of PMMA\textsuperscript{115, 116}; and the modification of polytetrafluoroethylene (PTFE) surfaces through refluxing with elementary sodium in toluene to generate double bonds, followed by an 8 h oxidation at 120 °C in a 1:1 mixture of trifluoroacetic acid and hydrogen peroxide (38%) to improve membrane wetting and the immobilization of the enzyme alliinase\textsuperscript{117}.

1.2.1.2.2 Ionised Gas Treatments

Chemical modification involving irradiation to partially decompose the surface or introduce other functional groups includes the deposition of organic\textsuperscript{118, 119, 120, 121} and inorganic\textsuperscript{122, 123, 124, 125} coatings, electrochemical or thermal oxidation\textsuperscript{126, 127}.
gas plasma treatments\textsuperscript{129, 130, 131, 132, 133}, surface cleaning, and sterilization procedures\textsuperscript{134}. Although wet chemical surface modifications are more capable of penetrating porous three-dimensional substrates than plasma and other energy source surface modification techniques\textsuperscript{135}, ionised gas treatments offer significant advantages of their own.

1.2.1.2.2.1 Plasma

Plasma is a high-energy state of matter, in which a gas is partially ionized into charged particles, electrons, and neutral molecules\textsuperscript{136}. Plasma can provide modification of the top nanometer of a polymer surface without using solvents or generating chemical waste, and with less degradation and roughening of the material than many wet chemical treatments\textsuperscript{137, 138}. However, the repeatability of results between different laboratories is complicated by the many parameters involved to optimize conditions, such as time, temperature, power, gas composition/flow/pressure, orientation of the reactor, and distance of the substrate from the plasma source. In addition, contamination is a major concern due to the possibility of introducing chemicals into the chamber other than those monomers and gases intentionally added, due to improper cleaning procedures.

Some examples of plasma modification of polymer surfaces include: the introduction of oxygen containing functional groups to polycaprolactone (PCL)\textsuperscript{139}, PE\textsuperscript{111}, and polyethylene terephthalate (PET)\textsuperscript{140}, the introduction of carboxyl groups with carbon dioxide plasma on PP\textsuperscript{141}, PS\textsuperscript{142}, and PE\textsuperscript{143}, and the use of air plasma to oxidize PMMA\textsuperscript{115}. Ammonia and nitrogen plasmas have also been used to impart amine groups to the surface of PTFE\textsuperscript{144}.
1.2.1.2.2.2 Corona Discharge.

Corona discharge is a continuous process in which an electrically induced stream of ionized air bombards a polymer surface. It acts to introduce a broad range of surface oxidation products rather than the specific products induced through plasma modification\(^{145}\). Because it does not operate under a vacuum, contamination may also be an issue, and variations in local temperature and humidity can affect consistency of treatment\(^{109}\). The stability of these oxidation products is also poor, creating the need for immediate use after treatment.

1.2.1.2.2.3 Flame Treatment.

Surface modification by flame treatment is similar to corona discharge; flame treatment is a non-specific surface functionalisation method that bombards the polymer surface with ionized air, generating a broad spectrum of surface oxidation products in the top several monolayers\(^{146}\). In this method, burning an oxygen rich gas mixture generates the reactive oxygen. Flame treatment has been shown to impart hydroxyl, aldehyde, and carboxylic acid functionalities to poly(ethylene) and is utilized to enhance printability, wettability, and adhesion. However, consistency and accuracy of flame temperature, contact time, and composition are difficult to control, and thus repeatability is difficult.

1.2.1.2.2.4 UV Irradiation

Surface modification with ultraviolet (UV) irradiation differs from ionized gas treatments because of the ability to tailor the depth of surface reactivity through the variation of the wavelength, leading to the control of the absorption coefficient. When exposed to UV light, polymer surfaces generate reactive sites, which can become functional groups upon exposure to gas or can be used to initiate UV-induced graft polymerization. However, in applications where the optical properties of the polymer are critical, UV treatment may not be ideal due to its ability to affect
the optical properties of the polymer. Also, debris on the surface of the polymer may act to block any UV treatment, leading to a lack of consistency.

Examples of where UV irradiation has been used include the introduction of carboxylic acid functionality to PMMA, as well as the activation of PS surfaces for enzyme immobilization and tissue engineering applications. UV irradiation has also been used to initiate radical graft polymerization of bioactive compounds.

1.2.1.2.2.5 Ion Implantation

Ion implantation surface modification involves accelerating ions to a particular energy and directing them toward a polymer surface, providing the advantage of creating a surface layer with desirable properties without detrimentally affecting the bulk properties. It has proven particularly attractive as a surface modification technique due to its flexibility, effectiveness, and environmentally friendly nature compared with conventional techniques. Also, the ion beam has proven more effective in modifying polymer surfaces than UV-light, γ-rays, X-rays, and electron beams. This is because energetic ions have a higher cross-section for ionization and larger linear energy transfer (LET, eV nm$^{-1}$) than these conventional radiation types of comparable energy, owing to their deeper range. Ion implantation has been successful in biomaterials modification, such as in improving the wear resistance of artificial joint components, in improving wettability, anticoagulability, and anticalcific behaviour of biomedical polymers, and in minimizing biofouling of medical devices.

Using this technique, there remains the possibility of creating atomic clusters. Atomic clusters are aggregates of a few to tens of thousands of atoms bound together by intermolecular forces, of either the same type or varying types. These aggregates share properties intermediate to those of individual atoms and solids, as they share discrete energy states and bulk matter characterised by bands of states. These clusters have low a penetrating power of typically 1-3 atomic layers. These
clusters account for a low percentage of the modification of the surface, and their
effect has been disregarded.

1.2.1.3 Biochemical Surface Modifications Of Biomaterials For Increased
Biocompatibility

Biochemical modification refers to the use of biochemical coatings, such as a
coating of extracellular matrix proteins\textsuperscript{153}, such as fibronectin, vitronectin, and
collagen to allow for the enhancement of interactions between the materials and
the cells through the promotion and regulation of cellular functions such as
adhesion, migration, proliferation, and differentiation\textsuperscript{154, 155}.

Two main classes of proteins have traditionally been immobilized on biomaterial
surfaces for different effects. The first class is adhesive proteins derived from the
ECM such as fibronectin, laminin, vitronectin, and collagen. Commonly used for the
promotion of cell adhesion and the enhancement of cell attachment via ligand–
acceptor interaction, adhesive peptides containing the Arg–Gly–Asp (RGD)
sequence are especially popular in this class\textsuperscript{156}. The second class of proteins that
are commonly immobilised on biomaterial surfaces are growth factors commonly
used for the control of cellular behaviours such as proliferation and differentiation.
Examples of this class include epidermal growth factor (EGF) immobilised on a
polystyrene plate to induce phosphorylation of the EGF receptor\textsuperscript{157}, which could, in
turn, be used to stimulate DNA synthesis in hepatocytes. Bone morphogenetic
protein (BMP) has also been immobilized on biomaterial surfaces to induce
differentiation of the bone cells\textsuperscript{158}.

A complication of biochemical modification arises when ensuring that the natural
conformation of the immobilised adhesive or growth protein is maintained. This
complication can be managed through various methods of immobilizing a bioactive
compound on a biomaterial surface, such as covalent attachment or non-covalent
immobilisation, including adsorption via electrostatic interactions or ligand–
receptor pairing. Electrostatic adsorption is sometimes useful in drug delivery applications\textsuperscript{159} and regenerable antimicrobial textiles\textsuperscript{160}. However, simply casting a protein solution on a hydrophobic surface can only yield an uneven and non-stable protein layer, and in some cases, cannot form any protein layer at all. Ligand–receptor pairing interaction is the strongest reported non-covalent bond, with an unbinding force of up to 250 pN\textsuperscript{161}. Covalent immobilization offers the most stable and reliable bond between the compound and the functionalized polymer surface, with its possible uses including the extension of a biomolecule's half-life, the prevention of its metabolism, or the continued bioactivity of in-dwelling devices. Examples include a stable collagen layer on a PLA surface created by treating PLA with ammonia plasma to increase hydrophilicity, followed by collagen coating\textsuperscript{162}, as well as collagen coated poly(ethylene terephthalate) (PET) film created by grafting poly(acrylic acid) on the PET film to produce a negatively charged surface, and then a coat of collagen via electrostatic interaction between the negatively charged PET surface and the positively charged collagen molecules\textsuperscript{163}.

Biochemical surface modifications have the disadvantage of often being time consuming and costly, with most of the described methods of surface modification requiring multiple processing steps, complex chemistries, and clean room facilities. Although features with sub-micrometer resolution are possible, the monolayer modifications that result are often too fragile to withstand physiological or micro-fluidic shear stresses, thereby limiting their long-term use in device applications\textsuperscript{79}.

1.3 Polysiloxanes

1.3.1 Introduction to the Field of Organosilicon Chemistry

Although Charles Friedel and James Crafts were the first to discover the first organosilicon compound, tetraethylsilane, in 1863 by reaction of tetrachlorosilane with diethylzinc\textsuperscript{164}, Mendeleev was the first to publish a prediction in 1891 that two
silicon atoms could attach to one oxygen atom to form a -Si-O-Si- linkage or an (O-Si-O)\textsubscript{x} system\textsuperscript{165}. Stokes went on to confirm Mendeleev's prediction in his study of the catalytic action of AlCl\textsubscript{3} on ethoxysilane in 1892\textsuperscript{166}. It was the chemist Frederick Kipping, however, who pioneered the first systematic study of the organosilicon compounds and organic compounds containing carbon silicon bonds a decade later, before the field of siloxane chemistry was born, earning him the title of father of organosilicon chemistry. He coined the term silicones in reference to these materials. His 1901-1905 publications formed the basis for the worldwide development of the synthetic rubber and silicone-based lubricant industries.

The next significant milestone in the development of the field occurred in the early 1940s, despite Kipping being quoted at a Bakerian lecture in 1936 as saying "the prospect of any immediate and important advance in this section of organic chemistry does not seem to be very hopeful". Hyde from the Corning Glass works, McGregor at the Mellon Institute, and Rochow at the General Electric Company, through their work on the synthesis and characterisation of silicones, discovered their thermal and thermo-oxidative stability, high chemical inertness, resistance to weathering, low surface tension, and the relatively weak dependence of their physical properties on temperature\textsuperscript{167}.

These results, as well as further developments of polysiloxane elastomers, resins and other products, led to the development of not just the industrial production of polysiloxanes in the 1940s, but also the first commercially available synthetic polymers with an inorganic main chain backbone.
1.3.2 Preparation of polysiloxanes

It would be beyond the scope of this work to comprehensively describe the preparation of the monomers that are used for various types of polysiloxane synthesis and the resulting synthesis of polysiloxanes, except to say that four major types of polymer forming reactions can prepare polysiloxanes. These include (1) hydrolysis of chlorosilanes; (2) equilibrium of lower siloxanes; (3) ring opening polymerization reactions; and (4) special condensation of polymerization reactions. Among these four reactions, the first and last are step growth polymerization processes, the second is a step growth redistribution process, and the third is a chain growth polymerization reaction. Equilibrium processes lead to the thermodynamic equilibrium between cyclic and linear siloxane molecules and also within each of these groups to form a distribution of molecular sizes. Equilibrium reactions are the most characteristic of the polysiloxane forming process, since, with few exceptions, they occur in each of the above four preparation processes.

This leads to a more precise term, being polymerized siloxanes or polysiloxanes, where silicones are a mixture of inorganic-organic polymers with the chemical formula \([R_2SiO]_n\), and R is an organic group such as methyl, ethyl, or phenyl. Polysiloxanes consist of an inorganic silicon-oxygen backbone (\(-\text{Si-O-Si-O-Si-}\)) with organic side groups attached to the silicon atoms. More comprehensive discussions can be found in a variety of organosilicon chemistry textbooks\(^{168,169}\).

1.3.3 Structural Properties of Linear Polysiloxanes

One of the most commonly noted macroscopic characteristics of siloxane polymers is their elasticity, both at low temperatures and at relatively high temperatures. Siloxanes can retain their elasticity for several thousand hours at temperatures up
to 200°C. The intermolecular interactions of the siloxane polymer that are responsible for its unusual elasticity are also responsible for the ease with which these polymers undergo viscous flow at low shear stress. This is reflected by: the low values of their activation energies; their Newtonian flow behaviour in constant viscosity - temperature measurements; their high rates of crystallisation on stretching; their very low glass transition temperature; and their high solubilities in non-polar solvents.

These structural properties are a result of weak secondary van de Waals attractive forces between neighbouring polymer chains, due to: the unusual flexibility of the Si-O-Si bond angles; the large differences in sizes of the alternating silicon and oxygen atoms; the relatively free rotation of the organic substituents around the C-Si bonds and the shielding of the main chain backbone by these pendant groups; the regularly coiled helical structures of polymer segments at low temperatures; and the large free volume between neighbouring chain segments.

1.3.4 Thermal Stability and Degradation Behaviour Of Linear Polysiloxanes In a Vacuum or an Inert Environment

One of the main characteristics of this family of polymers is the relatively high thermal and thermo-oxidative stability. While a majority of C-C single bond main chain polymers begin to degrade at ~200°C, due to the greater strength of the Si-O bond, purified polysiloxanes are stable under vacuum or inert atmospheres to 350-400°C. Impure samples containing ionic or catalytic amounts of nucleophillic impurities and varying types of polymer end groups can have a dramatic effect on the thermal and thermo-oxidative stability, both by lowering the onset of thermal degradation and also by completely changing the degradation mechanism itself.
Thus, it is important to maintain the highest quality siloxane possible when conducting experimentation.

At high temperatures, in an inert or vacuum atmosphere, the degradation of linear polysiloxanes produces volatile lower molecular weight products. The most common siloxane is linear polydimethylsiloxane (PDMS), as seen in Figure 4, and this is the silicone that we use in this work.

![Figure 4: General polysiloxane backbone structure for PDMS.](image)

For pure PDMS, purely thermal degradation in a vacuum or inert environment results in depolymerisation reactions to form lower molecular weight cyclic siloxy compound products with the general structural formula \([\text{CH}_3\text{SiO}]_n\), in which \(n\) has values from 3 through 20. The absence of char or other residue after thermal degradation implies that the mechanism responsible is the heterolytic cleavage of the Si-O main chain bonds by a depolymerisation reaction rather than the random...
homolytic thermal dissociation of the Si-C or the C-H bonds. This is in agreement with the thermal stability of tetramethylsilane in vapour phase, even at temperatures above 600°C.

However, as mentioned earlier, ionic or catalytic amounts of nucleophilic impurities and varying types of polymer end groups alter the temperature at which the material starts to thermally degrade and also the mechanism responsible. Three different mechanisms have been proposed, each contributing to siloxane re-arrangement, but occurring at different locations along the polymer chain.

The first of these mechanisms is the unzipping of the silanol-terminated polymer, proposed in 1968 by Aleksandrova and Rode. This occurs when the polysiloxane chains back-bite, undergoing a siloxane exchange and re-arrangement reaction to form a low molecular weight cyclic siloxy compound. In this case, six to eight member cyclic compounds would be the most prominent compounds due to their high rate of formation and thermal stability.

The second possible mechanism is the random chain scission of the trimethylsilyl end-capped polymer. This process involves depolymerisation by random attack on the siloxane units along the main chain, followed by an unzipping of the reactive fragments. This mechanism can occur at any position along the polymer chain through the formation of a loop within the chain backbone, and specific end groups or nucleophilic impurities are not required for its initiation.

The third thermal degradation mechanism describes the initiation of polysiloxane depolymerisation at the site of an external catalyst or ionic impurity. Such a mechanism results in the expulsion of lower molecular weight volatile species and
the formation of cross-linked cyclic siloxanes. Of course, it should be noted that further thermal degradation eventually yields pure silica, (SiO$_2$)$_x$.

**1.3.5 Thermo-Oxidative Stability and Degradation Behaviour Of Linear Polysiloxanes**

The degradation behaviour of polysiloxanes in air at low temperatures is much the same as that in a vacuum or inert atmosphere, with eventual decomposition into pure silica, (SiO$_2$)$_x$, with the inclusion of an additional weight loss step. This extra weight loss step corresponds to an expulsion of volatile free radicals and resulting decreases in the C/Si ratio, along with an increase in cross-linking due to the formation of Si-O-Si bridges.

Initially$^{170}$, oxygen reacts with the pendant organic groups, leading to the formation of hydrogen peroxide, which decomposes to form hydroxyl and silyl radicals, along with formaldehyde, which is a reported degradation product of thermo-oxidative degradation of PDMS. These two radicals combine to form a silanol group, which can either undergo a silanol condensation reaction to form cross-links with the expulsion of water by-products, or the different radicals can abstract a hydrogen atom from a methyl group$^{170}$. The methylene radicals can then undergo further reactions to form cross-links.

At higher temperatures, the main siloxy bonds can rupture, resulting in a degradation process more akin to that in a vacuum or inert atmosphere. It is salient at this point to mention that the thermo-oxidative stability of the polysiloxanes depends on the type of organic substituents bonded to the silicon atoms. Thus the stability of the polymer should, with the appropriate regard to purity, decrease as a function of structure in the order of the following monomers.

\[
\text{C}_6\text{H}_5 > \text{CH}_2 = \text{CH} > \text{CH}_3 > \text{C}_2\text{H}_5
\]
1.4 Ion Implantation of Poly-di-methylsiloxane (PDMS)

1.4.1 Theory of Ion Polymer Interactions: a Physical Investigation

Ion implantation of polymers is an attractive proposition because it allows for the modification and tailoring of the surface layer, both chemically and mechanically, while retaining the bulk properties of the polymer. This allows for the engineering of mechanical properties such as elasticity, hardness, Young’s modulus, and friction, but also surface activity properties which can be exploited for biomedical application such as “cytocompatibility improvement” [171], the creation of an “osteogenic environment” [172], “strong improvement of cell adhesion” [173], and an enhancement of differentiation [174]. Further, ion implanted engineered biopolymers have been also shown to induce anti-thrombogenic [175] and prevent infection responses [176].

These changes are effected by irreversibly changing the structure, composition, and properties of the surface layers of the polymer through ion implantation (irradiation). This is done in a combination of two processes, through doping or chemical effects by the introduction of implanted metal ion species and through irradiation induced defects. It is thus important to understand these damage mechanisms so as to better aid in the design of future functional materials. Irradiation induced defects are more important to the understanding of implantation of polymers than in either ceramics or metals. This is due to their relatively large free volume, often larger than 20%, and an atomic density that is relatively small compared to metals and ceramics, combined with weaker molecular bonds. Irradiation induced defects may even go so far as masking any doping effects, primarily for three reasons: firstly, any doping effects are an ‘end of track’ effect, and the implanted ion concentrations are inevitably very low compared to the induced structural and compositional changes to the polymer surface. Secondly,
bond breakage and chain scission of organic molecules results in the formation of a large group of lower molecular weight molecules, many of which may be volatile; and thirdly, there is a lesser ability to anneal out any damage resulting from the implantation process than in metals or ceramics.

When an accelerated ion is implanted into the polymer, the ion collides with the polymer atoms and loses energy by two main processes, either by interacting with target nuclei or by interacting with target electrons. Interaction with target nuclei is called nuclear stopping, and the interaction with electrons is electronic stopping. Thus, it is traditionally assumed that the energy transfer is the sum of these two stopping effects and modern computer models, such as SRIM (or the older version TRIM), result in good agreement with experimental results.\textsuperscript{177}

Nuclear stopping is the momentum transfer from ion to target atom with consideration for the interatomic potential between the two atoms. When the penetrating ion transfers energy greater than the displacement threshold energy to a target atom, nuclear scattering occurs. Otherwise, knock-on atoms cannot escape their equilibrium positions, and their energy dissipates as atomic vibrations (phonons). The atomic vibrations and phonon dissipation relate to localised heating. If the current density is too high, then the regions of localised heating due to the ion tracks will overlap, leading to overheating, and result in thermal and thermo-oxidative degradation. This is exacerbated by the absence of a good contact with a cooled substrate. For this reason, for the prevention of thermal degradation as a result of overheating, a recommended average current density of 1-10 µA/cm\textsuperscript{2} has been reported for irradiation in polymers.\textsuperscript{178}

Interactions with the electrons, both elastic and non-elastic, result from the electromagnetic interaction between the positively charged penetrating ion and the target electrons. Elastic interactions involve close collisions with large energy transfers, which are often referred to as knock-on collisions because, while they are very infrequent, each collision transfers a large amount of energy to a target
electron (>100 eV). These knock-on electrons are often referred to as secondary electrons. These energetic free electrons can penetrate deeper into the polymer than the penetration depth of the implanted ion, resulting in structural transformation in deep layers.

Inelastic interactions involve distant resonant collisions with small momentum transfer, which is often referred to as glancing collisions. Glancing collisions are much more frequent than knock-on collisions, but each collision involves a smaller energy transfer (< 100 eV) than for knock-on collisions. Both glancing and knock-on collisions transfer energy through electronic excitation and ionization. Electronic excitation is the process in which an orbital electron is raised to a higher energy level, whereas, ionization is where an orbital electron is ejected from the atom. All excited electrons (plasmons) eventually lose energy through heating of the surrounding matter. A cascade of collisions will result if the recoiling atoms or electrons have enough kinetic energy, resulting in a series of defects in the polymer structure that are confined to a tear drop shaped volume, with the narrowest point at the surface, which is called the spur of the penetrating ion (Fig 5). It should be noted, however, that at the implantation energies used in this work, low keV, the electronic stopping energy dominates – accounting for around 98% of all collisions.

An important parameter to introduce here then is the energy deposited per unit ion path length or linear energy transfer (LET). This implies the continuous slowing of an ion due to energy loss, leading to a cylindrical path that marks the passage of the ion. In reality, energy deposition into the polymer medium occurs discretely in spurs as above, not continuously. However, in the discussion of ion – polymer interaction, it is useful to designate a continuous column of energy deposition when a positively charged ion passes through a medium. This process allows for the definition of two important values, $R_c$ and $R_p$. $R_c$ is the range of uncertainty in energy deposition at the time of the initial energy deposition energy density within the core, which is mostly due to glancing collisions and a small fraction of low energy knock-on electrons which are trapped inside the core, while $R_p$, the
penumbra radius, is the range of secondary electrons. Extensive modelling of both are provided by Chatterjee and Schafer\textsuperscript{179, 180}.

Figure 5: Penetration of Ni ions (red) into PDMS. The ion track (Red) triggers cascading collisions other constituent atoms within the solid polymer, H (green), C (blue), O (magenta) and Si (light blue).

Linear energy transfer is an important concept to consider because when the electronic LET is high, there is an increased production of active chemical species, cations, anions, radicals, and electrons along the polymer chains. Coulombic attraction and repulsion among these active species cause violent bond stretching and segmental motion in the polymer chains, which can then lead to cross-linking as well as bond breakage\textsuperscript{181}. The cross-linking acts to increase the molecular weight, hardness, and wear resistance. Incomplete reactions of these free radicals may drastically increase chemical reactivity and thus promote detrimental oxidation, which leads to a degradation of mechanical strength.

While both nuclear and electronic energy transfer can result in scission as well as cross linking, nuclear stopping is more likely to results in chain scission, while electronic stopping has a greater chance of inducing cross-linking. The magnitude of
ionisation within the polymer as a result of irradiation varies with ion velocity and charge state. So, to maximise the interaction and thus the impact of irradiation, it is advantageous to use large atomic number ion species and implant with high-energy ions, so long as the velocity of the ion is not too large. High velocity ions have short interaction times, leading to a small stopping power and large $r_c$ and $r_p$.

From the rate of energy loss of the energetic ion within the medium, a range and Bragg curve, that is the energy attenuation as a function of distance within the medium, can be calculated. Fig 6 shows the Bragg curve for an alpha particle in air. As seen in Figure 6, most of the energy loss occurs near the end of the particle’s path length where the speed is smallest, resulting in a pronounced peak, also known as the Bragg peak. This phenomenon is particularly relevant for therapeutic applications where it is desirable to irradiate specific areas while minimising the damage to surrounding tissues.

![Figure 6: Energy loss for 5.49 MeV alpha particles in air with characteristic Bragg peak.](image-url)
1.4.2 Ion Implantation of PDMS: a Chemical Investigation

Immediately following the metal ion implantation of the surface, the PDMS surface becomes altered and covered by what appear to be stress induced V-shaped cracks, which penetrate deeply into the elastomer matrix. It is well known and has been demonstrated that V-shaped cracks tend to open up on the surface as a method of strain relief, and the frequency of these V-shaped cracks increases with strain induced by increased implantation dose. It is well understood that the bombarding of the PDMS surface with energetic metal ions, the mechanism of which has been described above, acts to thermo-oxidatively degrade the organic methyl (CH$_3$) groups, and to cut and densify the siloxy backbone (Si-O-Si) of the elastomer and its side chains, leading to the release of volatile species and a marked increase in the concentration of carbides, hydroxides, and oxygen rich silicon species such as silanol (Si-OH) on the surface. The mechanism of this has been described above and is a partial degradation, since the stiff layer is not pure silica. These oxidative chemical transformations give rise to a stiff, hydrophilic silica-like surface film that varies in thickness, depending upon the dose and metal ion species of the ion implantation process$^{70}$. It should be noted that this chemical transformation is a surface process, penetrating ~250 nm into the polymer and that the underlying elastomer base remains unaffected and elastic in nature.

After the implantation process, over time, the lower molecular weight molecules (LMW) formed during implantation at various depths within the ion range will diffuse back to the surface from the elastomer bulk. The diffusion time is influenced by both the thickness of the surface layer, due to much shorter diffusion times and smaller volumes, to serve as a LMW repository, and also to the thickness of the metal-rich layer acting as a barrier for diffusion$^{182}$. This causes the silica-like layer to undergo compressive stress compared to the elastomer base.

Due to the stiff, silica-like surface having a much higher stretching rigidity than the elastic foundation, both the stiff, silica-like skin and the unmodified elastic
elastomer base respond to the resulting non-equilibrium stresses that result by minimizing their bending and stretching energies. This leads to a wave-like regular pattern of undulations in various size and shapes in complex coherent and semi-coherent domains, which are constituted by differing orientations of the waves that are formed. These wrinkling domains completely cover the surface of the film and fill in the space between the surface cracks, as a result of the competition between the skin’s bending response and the substrate’s elastic restoration. A more in-depth discussion of the nature of buckling follows.

1.4.3 Classical Theory of Buckling

In the previous section, we have shown that the surface of a thick polydimethylsiloxane (PDMS) film decomposes as a result of the energetic ions impacting on the surface layer, creating a stiff silicon- and oxygen-rich layer. The stiff layer adheres to an unchanged elastomer base, where the thickness of the stiff layer, and the depth and thickness of the implanted metal layer depend on the penetration depth and dose of the implanted ions. The silica-like stiff film suffers from compressive stress while still being coupled to the underlying elastomeric matrix, so the resulting biaxial compressive stress on the thin stiff film leads to buckling, buckle-driven delamination, and/or fracture.

This lateral force mismatch between the adhered stiff skin and the elastomer matrix, which is confined to a rigid silicon base, is what leads to surface undulations in the form of buckles as the stiff skin undergoes compressive stress. To accommodate the induced mismatch strain between the skin and the elastomer substrate, and to minimize the total elastic energy in the film and the substrate\textsuperscript{183}, the skin buckles in a wave-like manner, forming different stress relief patterns.

The buckling wavelength $d$ arises from the buckling instability and can be calculated as\textsuperscript{184}. 
\[ d = \alpha h \left( \frac{E_f}{E_s} \right)^{1/3} \]

where \( h \) is the film thickness, \( E_f \) and \( E_s \) are the instantaneous elastic moduli of the silicon- and oxygen-rich film and the elastomer substrate, respectively, and \( \alpha \) is a unitless prefactor equal to \( 2\pi[(3-\nu_m)(1+\nu_m)/12]^{1/3} \). For silicone with a Poisson ratio, \( \nu_m \), of 0.5 and modulus of 0.5 MPa, and a film of modulus 3.2 GPa, using the wavelengths measured with optical microscopy, from 2.2 \( \mu \)m to 20 \( \mu \)m, a thickness of 2.7 nm - 250 nm is calculated, dependent on dose and metal ion species.

The classical relationship for buckling of a linear elastic stiff skin with modulus \( E_f \), attached to a compliant substrate with elastic modulus \( E_s \), gives the critical strain associated with the onset of instability as \( e_c \approx \frac{1}{4 \left( 3 E_s / E_f \right)^{2/3}} \). This figure is independent of the skin thickness; it is only influenced by applied strain as a result of the compressed silicon and oxygen rich layer.

This now allows us an analytical prediction for the amplitude (A) of the wrinkles under uniaxial strain, which is given as

\[ A = h \left( \frac{e_{pre}}{e_c} - 1 \right)^{1/2} \]

where, again, \( h \) is the film thickness, \( e_{pre} \) is the prestrain and \( e_c \) is the critical buckling strain. In this work we have not used any prestrain when buckling the films with metal ion implantation.

It should be noted however that, in proportion to the film thickness and as a non-dimensional function of the prestrain and critical strain for buckling, the compressive stress decreases to zero at the edge of a buckled region, leading to a flat region of zero buckling. This region can be extended or decreased to zero and is potentially useful when designed into a larger scale buckled system where planarity is required for useful applications. It has been suggested that potential uses could include efficient photodetection or other functions.
Usually associated with highly constrained stiffer substrates, leading to high critical stresses for wrinkling, buckling deformation of the film is also witnessed in combination with buckling in this system. The substrate constraint may be locally alleviated by interfacial defects that lead to partial delamination of the film. In this case, the delaminated portion of the film buckles, which in turn drives growth of delamination through interfacial fracture\(^1\). Through co-development of both buckling and delamination, abundant and complex buckling patterns are formed, most commonly as telephone-cord patterns in a hooping pattern, and at high doses, a boundary of pillars at the edge of islands. A schematic of both buckling and buckle delamination is shown in Figure 7.

![Schematic](image)

Figure 7: Schematic of a) unbuckled PDMS elastomer film on a rigid Si base b) buckling, wrinkling without interfacial delamination, constrained on a Si base, and c) buckle delamination, wrinkling with interfacial delamination, constrained on a Si base.

While providing an approximate explanation for what is occurring, the system in this work is further complicated by the depth and thickness of the volume of metal
carbon functional groups with complex chemistries that result from the implantation process and any geometric confinement induced through the use of masks. This ensures that the classical model discussed above loses its accuracy in terms of calculating the wavelength and the amplitude of the surface buckling. In all cases physical measurement via optical microscopy is used rather than a calculation based on the theoretical modelling of the buckling system.

1.4.4 Buckling in PDMS

The ability to pattern the surfaces of bulk materials and thin films allows for the creation of technological and scientific designs through opportunities to array, compartmentalize, interconnect, and parallelize physical, chemical, and biological functions. Potential or actual scientific and technological applications include: micro-fluidics, micro-electromechanical system devices, high-throughput approaches in materials synthesis, catalyst discovery, chemical and biological sensing, genomics, drug screening\textsuperscript{192, 193}, and proteomics\textsuperscript{194, 195}. When large scale patterning at small length scales is included, examples can include a variety of applications such as studies of small-volume (e.g., atto-liter) chemistry and single-molecule biophysics\textsuperscript{196, 197, 198, 199}, stochastic sensing\textsuperscript{200}, biological pattern formation and recognition\textsuperscript{201, 202}, the functional consequences of cell shapes in development and stem-cell differentiation\textsuperscript{203, 204}, and the physics of photonic crystals\textsuperscript{205, 206}.

It has been common to utilise methodologies that have been developed from the semi-conductor industry, such as photolithography-based methods or substrate pre-patterning with biochemical coatings. Besides both techniques being time consuming and costly, both methods, when used for selective patterning, often require multiple processing steps, complex chemistries, and clean room facilities. While features with sub-micrometer resolution are possible for both, the biomedical coating monolayer modifications that result are often too fragile to withstand physiological or micro-fluidic shear stresses, thereby limiting their long-
term use in device applications\textsuperscript{79}. For nanometer scale patterning, a variety of
direct deposition methods, including electron-beam lithography\textsuperscript{207}, atomic-force
microscopy–based dip-pen nanolithography\textsuperscript{208, 209}, and resist-deformation-based
nano-imprint lithography\textsuperscript{210} are commonly used. The following references provide
good reviews of these techniques\textsuperscript{211, 212, 213, 214}.

Surface buckling or wrinkling creates 3D relief structures that are complex,
coherent or semi-coherent, and have a dominant periodicity. They can be
generated in a variety of systems that include: thermally or mechanically stressed
metallic\textsuperscript{186,215}, polymeric\textsuperscript{216, 185}, and silicate\textsuperscript{217, 218, 219} thin films supported on
elastomeric substrates, and dried thin films prepared by the sol-gel method\textsuperscript{220, 221},
as well as soft gels placed under geometric confinement that are swollen\textsuperscript{222} or
dried\textsuperscript{223}.

Of interest to this study, is the buckling of an elastomer thick film. The ease with
which dominant and complex patterns can be generated and controlled on the
surface of the elastomer makes surface buckling an easy ‘bottom up’ way of using a
self-organising buckling effect to create and tune different topological structures on
the submicron to micrometer scales\textsuperscript{224, 52, 225} for scientific and technological
applications. This potentially provides a simple and inexpensive technique for rapid
and reproducible surface patterning, without the need for any pretreatment of the
elastomer such as stretching or coating. Recent techniques to create 3D regular
self-organised surface features on micron and submicron scales via buckling of
PDMS surfaces include plasma treatment and oxidation\textsuperscript{218, 226, 227, 228}, metal
deposition\textsuperscript{186, 229, 230}, ion beam irradiation\textsuperscript{52, 224, 231}, and ionising radiation\textsuperscript{232}.

An advantage of metal ion implantation over other methods used to buckle the
surface of elastomers is that it results in micron-sized features that are rich in
specific elements. As well as for its usefulness in controlling the topographical
regimes of buckling, metal ion implantation was chosen because it can also further
functionalise the surface. Previous work has shown that topography affects the
elemental properties\textsuperscript{233}, as such metal ions can also be used to introduce desired functional behaviour into the 3D self-organised surface features. This has led to the creation of ferroscaffolds with unique topographical formations, which hold enormous potential as stimulus-responsive drug carriers and scaffolding materials for tissue engineering. Hu et al. found that the magnetic sensitivity of ferroscaffolds exhibited different degrees of magnetism, which could be further used to control growth factors for cell cultures\textsuperscript{234}. A similar behaviour within the range of the buckling features can be expected when combining surface buckling with elemental functionalisation through metal ion implantation.

This work investigates a new mechanism for producing similar buckling behaviour to that reported previously for other methods, based on low energy metal ion implantation past a critical dose.
Part 2: Experimental

Chapter 2: Material Preparation, Modification and Characterisation

2.1 PDMS Processing

A series of identical, unstrained, homogeneous, and optically transparent high-quality 4-µm-thick PDMS films were created by spinning a liquid silicone mixture with a standard base-to-catalyst ratio of 10:1 (Sylgard-184, Dow Corning) onto a (1 1 1) single-sided polished silicon wafer (obtained from Solar Wafers) for 120 s at 8000 rpm. The surfaces of the PDMS films were inspected by scanning electron microscopy (SEM) and atomic force microscopy (AFM), and their aspect was smooth, homogeneous, and featureless. This lack of features appeared to be stable over time, as evidenced from inspecting the PDMS film surface over a period of days and weeks, Figure 8 schematically outlines the creation process of these films in preparation for modification.

Figure 8: Schematic of the manufacturing process for the creation of featureless, homogeneous thick PDMS films

2.1.1 PDMS Mixing and Degassing

PDMS is a material that is commonly used in a variety of scientific and technological applications, where it is possible to replicate vertical features of less than 2 nm.235
and lateral features of the order of 30 nm\textsuperscript{236} in PDMS. PDMS is widely available from a variety of manufacturers including Wacker, Dow Corning, NuSil, Rhodia, and GE Silicone\textsuperscript{237}, with Dow Corning's Sylgard 184 being the most common and reported to have been used with a base catalyst ratio ranging from 6:1 to 30:1\textsuperscript{238}, depending upon the application. However, the controlled mixing and gassing step is widely seen as unimportant in the fabrication of silicone moulded parts or membranes, as reflected by most authors in the literature, who merely quote the base catalyst ratio and describe the PDMS solution as mixed thoroughly. In this work, base/catalyst ratios of 10:1 and 20:1 were carefully measured and mixed thoroughly with a paddle pop stick.

Like mixing, there is a lack of detail, and indeed agreement, surrounding the commonly described degassing step. Since bubbles are visible in the PDMS solution, most researchers are most likely just concerned about removing all evidence of bubbles, without worrying about optimal vacuum timing or pressure values. The degassing step in this work involved allowing the liquid PDMS solution to sit inside a cool vacuum oven until all evidence of bubbles had been removed (10 min in this case).

\textbf{2.1.2 PDMS Membranes: Spin Coating and Curing}

Degassed liquid PDMS solution was spun onto a Si (1 1 1 ) wafer in order to create a membrane with a thickness on the order of 5 µm. A variety of peak spin times and speeds were trialled to optimise the thickness and homogeneity of the films (Fig. 9), with ramping steps used, as seen below in Figure 10, with 120 s at 8000 rpm eventually chosen for the main spin stage.
Figure 9: Cross-sectional SEM of the unmodified PDMS thick film on supporting Si wafer under different spinning conditions. A) 4000rpm for 60s b)8000 rpm for 120s.

Figure 10: Chosen spin-coating program for the manufacture of homogeneous, optically transparent films of PDMS on Si wafers ready for metal ion implantation.

As stated previously, the structure of PDMS is a cross-linked network of polymer chains that presents mostly an amorphous structure. These polymer chains are small, with a diameter of about 0.7 nm, and they are normally present in the polymer matrix as random coils with a diameter of 10 nm. These features are approximately an order of magnitude smaller than the thickness of the spun membrane supported on the Si wafer. As such, it is common to treat PDMS membranes as bulk material rather than dimension dependent, so far as mechanical or thermal stability are concerned. However, it is well known that dimension-dependent material properties such as strength have been identified in metallic materials, although this is primarily the result of dimension-dependent
crystal structures such as grain boundaries and surface-induced dislocation slipping barriers, which are lacking in polymer membranes.

It has recently been reported\textsuperscript{241}, however, that the reordering of polymer chain coils in PDMS membranes as a result of the high shear forces associated with high rpm forms stronger cross-linked networks, and thus greater mechanical strength and higher thermal stability. It is for this reason that the fabrication conditions of the PDMS membranes in this work were kept uniform.

After the liquid PDMS solution was thoroughly mixed, degassed, and spun onto a supporting Si wafer, appropriate curing conditions needed to be determined. While Dow Corning suggests curing at room temperature over 48 hours, 45 minutes at 100\textdegree C, 25 minutes at 125 \textdegree C, or 10 minutes at 150 \textdegree C, researchers have used a variety of alternate curing conditions. PDMS membranes in this work were cured on a hotplate for 90 minutes at 80\textdegree C.

Table 2: Recently reported PDMS curing conditions.

<table>
<thead>
<tr>
<th>Temperature (\textdegree C)</th>
<th>Time (min)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>65</td>
<td>120</td>
<td>242</td>
</tr>
<tr>
<td>65</td>
<td>300</td>
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<td>100</td>
<td>30</td>
<td>247</td>
</tr>
<tr>
<td>120</td>
<td>60</td>
<td>248</td>
</tr>
</tbody>
</table>
2.2 Metal Ion Implantation (MEVVA)

Using a Metal Vapour Vacuum Arc (MEVVA) ion source is a common method for generating metal ions\textsuperscript{249}. Metal plasma is produced by the vacuum arc discharge from microscopic cathode spots. Cathode spots are highly energetic emitting areas created by an arc evaporation process beginning with the striking of a high current, low voltage arc on the surface of a cathode. The localised temperature at the cathode spot is extremely high (~15000 °C), which results in a high velocity (10 km/s) jet of vaporised cathode material, leaving a crater behind on the cathode surface. The cathode spot is only active for a short period of time, before it self-extinguishes and re-ignites in a new area close to the previous crater. After ignition by a high voltage spark, the vacuum arc plasma is maintained between cathode spots and the anode. Material is vaporized from the cathode spots and feeds the discharge. The ionisation behaviour in the region of the cathode spots mainly defines the arc plasma parameters. No hot filaments or ambient gases are necessary for generation of the metal plasma.

The arc has an extremely high power density, resulting in a high level of ionization of between 30-100%, multiple charged ions, neutral particles, clusters, and macro-particles (droplets). If a reactive gas is introduced during the evaporation process, dissociation, ionisation, and excitation can occur during interaction with the ion flux, and a compound film will be deposited. For vacuum arc ion sources this provides an attractive option for high current, broad beams of metal ion species from throughout the periodic table, as well as other conducting solid materials.

When using a MEVVA source, an intense, highly ionised metal plasma plume is created at the vacuum arc cathode spot. The ion beam is extracted from this plume through a process of ion beam formation, which is schematically shown in Figure 11. Quasi-neutral plasma originally plumes away from the cathode and toward a
small gap in the anode. In the post-anode region a set of grids based on the acceleration, deceleration principle comprises the final ion beam extraction process, generating an ion beam that can then be used experimentally.

Figure 11: Schematic of a MEVVA source with a cathode - anode arc discharge, trigger for starting the arc, and three-grid extraction system.

One disadvantage to the arc evaporation process is that if the cathode spot stays at an evaporative point for too long, it can eject a large amount of macro-particles or droplets. These droplets are detrimental to the performance of the coating, as they are poorly adhered and can extend through the coating. If the cathode target material has a low melting point, the outcome can become even more problematic, as it is possible for cathode spots to evaporate through the target, resulting in either the target backing plate material being evaporated or cooling water entering the chamber.
Also, since the minimum value of stable arc current at the cathode spot is relatively high at several or even several tens of amperes\textsuperscript{250}, the problem of decreasing the beam current and thus preventing breakdown within the extraction gap becomes more important. So, to have a suitable value of average beam current and to reach good conditions for control of the beam current, most vacuum arc ion sources are operated in a repetitively pulsed mode. In the normal mode of vacuum arc ion source operation, the source can provide a few hundred mA of ion current, with the pulse length typically 0.2–1.0 ms. Steady-state operation of the source is also possible and may be used if one needs a very large area beam\textsuperscript{251}.

### 2.2.1 Operation of Equipment and Production of Samples

In the normal mode of operation, the ion beam contains ionisation states between $Q = 1^+$ and $Q = 5^+$\textsuperscript{252, 253}, depending on the metal used for the cathode of the vacuum arc, and these unwanted charge states are sometimes magnetically filtered out according to the desired application. In this work, the unstrained, homogeneous, optically transparent, spin coated 4 µm films of PDMS on Si wafers were ion implanted using a metal vapour vacuum arc ion source with a variety of metal targets at 45 kV and 80 mA, without any magnetic filtering. This meant that a variety of charged states of metal ions were available to chemically and physically interact with the polymer surface, as seen in Table 3.
Table 3: Sputtering Charge Probability (%)\textsuperscript{253}.

<table>
<thead>
<tr>
<th>Implanted Ion</th>
<th>Z</th>
<th>1+</th>
<th>2+</th>
<th>3+</th>
<th>4+</th>
<th>5+</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>12</td>
<td>46</td>
<td>54</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si</td>
<td>14</td>
<td>60.8</td>
<td>39.2</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>Ti</td>
<td>22</td>
<td>9.8</td>
<td>78</td>
<td>12.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>26</td>
<td>24.1</td>
<td>69.7</td>
<td>6.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co</td>
<td>27</td>
<td>27.9</td>
<td>71.7</td>
<td>0.44</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni</td>
<td>28</td>
<td>24.5</td>
<td>74.7</td>
<td>0.77</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eu</td>
<td>63</td>
<td>0.65</td>
<td>88.9</td>
<td>10.5</td>
<td>2.7</td>
<td>0.11</td>
</tr>
<tr>
<td>Ta</td>
<td>73</td>
<td>1</td>
<td>21.7</td>
<td>61.1</td>
<td>16.1</td>
<td>0.11</td>
</tr>
<tr>
<td>Au</td>
<td>79</td>
<td>12.5</td>
<td>77.8</td>
<td>9.6</td>
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</tr>
</tbody>
</table>

It is predictable then that the different ionisation charge states allow for different penetration ranges within the surface of the polymer, as calculated by SRIM from 54 nm to 210 nm (Table 4).

Table 4: Ion penetration ranges of different ionisation charge states in PDMS (nm).

<table>
<thead>
<tr>
<th>Implanted Ion</th>
<th>Z</th>
<th>1+ (45keV)</th>
<th>2+ (90keV)</th>
<th>3+ (135keV)</th>
<th>4+ (180keV)</th>
<th>5+ (225keV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg</td>
<td>12</td>
<td>152</td>
<td>310</td>
<td>475</td>
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<tr>
<td>Si</td>
<td>14</td>
<td>115</td>
<td>224</td>
<td>334</td>
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<tr>
<td>Ti</td>
<td>22</td>
<td>86</td>
<td>161</td>
<td>235</td>
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<tr>
<td>Fe</td>
<td>26</td>
<td>77.8</td>
<td>143.2</td>
<td>209.5</td>
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<tr>
<td>Co</td>
<td>27</td>
<td>77.1</td>
<td>141.3</td>
<td>206.9</td>
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<tr>
<td>Ni</td>
<td>28</td>
<td>77</td>
<td>142.1</td>
<td>208.8</td>
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<tr>
<td>Eu</td>
<td>63</td>
<td>56.5</td>
<td>88.7</td>
<td>117.9</td>
<td>145</td>
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<tr>
<td>Ta</td>
<td>73</td>
<td>57</td>
<td>88</td>
<td>115.5</td>
<td>142</td>
<td>167</td>
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<tr>
<td>Au</td>
<td>79</td>
<td>54</td>
<td>82</td>
<td>107</td>
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</table>

This allowed for the generation of a series of PDMS films that were implanted with a variety of metal ions, including Au, Fe, Ni, Co, Mg, Eu, and Ti at a variety of timed exposures, as shown in Table 5. A diverse range of characterisation techniques were then used to investigate the chemical and morphological changes that resulted. Details of these characterisation methods follow. Both silicon implanted reference samples and films partially covered with Al foil were also created.
Table 5: List of samples created, with ion elemental species used and times of exposure in seconds. All ion implanting was done on an approx. 4µm thick PDMS film on a supporting Si wafer.

<table>
<thead>
<tr>
<th>Mg</th>
<th>Si</th>
<th>Ti</th>
<th>Fe</th>
<th>Co</th>
<th>Ni</th>
<th>Eu</th>
<th>Ta</th>
<th>Au</th>
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</tbody>
</table>

2.3 Surface Characterisation Techniques

2.3.1 Microscopic Surface Characterisation Techniques

2.3.1.1 Transmission electron microscopy (TEM)

Transmission electron microscopy (TEM) is a microscopy technique involving the transmission of a beam of electrons through an ultra-thin specimen, often prepared via focused ion beam (FIB), resulting in interaction between the electron beam and the specimen. A cross-sectional image is formed from the interaction of the electrons transmitted through the specimen, which can then be magnified, focused, and captured. TEMs are capable of imaging at a significantly higher resolution than light microscopes, owing to the small de Broglie wavelength of electrons of 1.23 nm. This allows for the investigation of fine detail, down to tens of thousands of times smaller than the smallest resolvable object in a light microscope.
A TEM microscope contains several components, including a vacuum system, to allow for the voltage difference between the cathode and the ground without generating an arc, and to reduce the collision frequency of electrons with gas atoms to negligible levels: this effect is characterized by the mean free path; an electron emission source for the generation of the electron stream; a series of electromagnetic lenses, which are designed to act in a similar way to optical lenses, by focusing parallel rays at some constant focal length; and finally, the apertures, annular metallic plates through which electrons that are further than a fixed distance from the optical axis may be excluded. These each consist of a small metallic disc that is sufficiently thick to prevent electrons from passing through the disc, whilst permitting axial electrons.

This passage of only central electrons in a TEM causes two effects simultaneously: firstly, apertures decrease the beam intensity as electrons are filtered from the beam, which may be desired in the case of beam sensitive samples. Secondly, this filtering removes electrons that are scattered to high angles, which may be due to unwanted processes such as spherical or chromatic aberration, or due to diffraction from interaction within the sample. Imaging devices are then used to create an image from the electrons that exit the system. This cross-sectional image is useful in probing the structural and chemical changes as a result of surface modification.

In this work, a cross-sectional analysis was done on three samples: 1200s Fe implanted; 1200s Ni implanted, and 1200s Au implanted films. The Focused Ion Beam (FIB) lift-out technique was used to prepare the thin cross-sectional pieces of the film in preparation for cross-sectional TEM. This is where the surface of the film is coated by a conductive layer, in this case platinum, and then a thin membrane is milled and plucked out, ready for cross-sectional TEM.
2.3.1.2 Scanning Electron Microscopy (SEM)

The scanning electron microscope (SEM) is a type of electron microscope that images the sample surface by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample, producing signals that contain information about the sample's surface topography, composition, and other properties such as electrical conductivity. Images are then created from signals resulting from interactions between the electron beam and atoms at or near the surface of the sample.
In the most common or standard detection mode, secondary electron imaging (SEI), the SEM can produce very high-resolution images of a sample surface, revealing details less than 1 to 5 nm in size. A wide range of magnifications is possible, from about 10× to more than 500,000×, due to the large depth of field in SEM resulting from the very narrow electron beam. Back-scattered electrons (BSE) are beam electrons that are reflected from the sample by elastic scattering. BSE are often used in analytical SEM and provide another common SEM imaging mode. Because the intensity of the BSE signal is strongly related to the atomic number (Z) of the specimen, BSE images can provide information about the distribution of different elements in the sample.

While SEM is not as surface sensitive as other imaging techniques, and non-conducting polymers must be sputter-coated prior to analysis, it is one of the more widely available tools in surface analysis. It has been used to examine cell adhesion on biocompatible and hemocompatible materials, and the efficacy of tissue engineering scaffolds.

SEM operates when the electron beam, which typically has an energy ranging from 0.5 keV to 40 keV, is focused by one or two condenser lenses to a spot about 0.4 nm to 5 nm in diameter. The beam then passes through pairs of scanning coils or pairs of deflector plates in the electron column, typically in the final lens, which deflect the beam in the x and y axes so that it scans in a raster fashion over a rectangular area of the sample surface.

When this primary electron beam interacts with the sample, the electrons lose energy by repeated random scattering and absorption within the interaction volume, a teardrop-shaped volume of the specimen. Atomic interactions between the electron beam and the sample result in the reflection of high-energy electrons by elastic scattering, emission of secondary electrons by inelastic scattering, and
the emission of electromagnetic radiation, each of which can be detected by specialized detectors. Electronic amplifiers of various types are used to amplify the signals, which are displayed as variations in brightness on a cathode ray tube (CRT). The raster scanning of the CRT display is synchronized with that of the beam on the specimen in the microscope, and the resulting image is therefore a distribution map of the intensity of the signal being emitted from the scanned area of the specimen.

In this work, SEM imaging and EDS were conducted on PDMS films implanted with Ni, Co, Fe, Eu, and a combination of these elements, all exposed for 900 s. This was also done for Co and Fe samples exposed for 60 s, 90 s, and 180 s. SEM was not the primary tool to study the effects of wrinkles and surface cracking due to the limited depth of field making surface features relatively difficult to see when compared to optical imaging and AFM. SEM and EDS of the aforementioned samples were conducted without any surface coating.

### 2.3.1.2.1 Field Emission Scanning Electron Microscope (FESEM)

The field emission scanning electron microscope (FESEM) is similar to regular SEM except in the case of the electron gun. The primary function of the electron gun is to provide a stable beam of electrons. This can be done in two ways, with the use of a thermionic emitter or a field emitter.

Thermionic emitters use an electrical current to heat up a filament, the two most common types being either tungsten (W) or lanthanum hexaboride (LaB$_6$). When the heat is enough to overcome the work function of the filament material, the electrons can escape from the material, thereby generating a beam of electrons. Thermionic emitters are relatively inexpensive and need no special vacuum. However, they have low brightness, limited lifetimes due to the evaporation of cathode material, and large energy spreads.
Field emission is one way of generating electrons that avoids these problems. A field emission source does not heat the filament. A field emission microscope consists of a metallic sample in the form of a sharp tip and a conducting fluorescent screen enclosed in ultra-high vacuum. The tip radius used is typically of the order of 100 nm. The sample is held at a large negative potential (1-10 kV) relative to the fluorescent screen. This gives an electric field near the tip apex of the order of $10^{10}$ V/m, which is high enough for field emission of electrons to take place.

The field-emitted electrons travel along the field lines and produce bright and dark patches on the fluorescent screen, giving a one-to-one correspondence with the crystal planes of the hemispherical emitter. The emission current varies strongly with the local work function, in accordance with the Fowler-Nordheim equation\textsuperscript{259,260}; hence, the FESEM image displays the projected work function map of the emitter surface. The closely packed faces have higher work functions than atomically rough regions, and they thus show up in the image as dark spots on a brighter background. In short, the work function anisotropy of the crystal planes is mapped onto the screen as intensity variations.

FESEM uses a field emission source producing a cleaner image, less electrostatic distortion, and spatial resolution < 2 nm, as compared to regular SEM. Here, FESEM was used to investigate the surfaces on both Au coated Fe implanted PDMS films with 900 s exposure and uncoated Ni and Eu/Ni implanted films with a 900 s exposure time. Due to charging of the insulating surface, the resolution was limited for the uncoated surfaces.
2.3.1.3 Atomic Force Microscopy (AFM)

Atomic force microscopy (AFM) is a very high-resolution type of scanning probe microscopy, generating 3D images to resolutions of a fraction of a nanometer. Information is gathered through very precise scanning by "feeling" the surface with a mechanical probe by using piezoelectric elements that facilitate tiny, but accurate and precise movements on (electronic) command, as seen schematically in Figure 13. AFM can operate with a resolution of thirty by less than one angstroms (lateral by vertical)\(^{109}\). Surface roughness is an important parameter in biomedical materials, as it may affect cell adhesion\(^{261}\). In the case of vascular prostheses, increased surface roughness can compromise hemocompatibility, as turbulent blood flow may initiate hemolysis\(^{255}\).

![Figure 13: Schematic representation of the key parts and functions of an AFM\(^{262}\)](image-url)
The AFM (Fig 13) consists of a cantilever, typically silicon or silicon nitride, with a tip radius of curvature on the order of nanometers or smaller at the end that is used to scan the specimen surface, as it is moved by a lead zirconate titanate (PZT) scanner. When the tip is brought into proximity to a sample surface, forces between the tip and the sample lead to a deflection of the cantilever according to Hooke's law, allowing for the measurement of a variety of forces such as the mechanical contact force, van der Waals forces, capillary forces, chemical bonding, electrostatic forces, magnetic forces, Casimir forces, and solvation forces. Hooke's law gives $F = -kz$, where $F$ is the force, $k$ is the stiffness of the lever, and $z$ is the distance the lever is bent. The deflection of the cantilever is measured using a laser spot reflected from the top surface of the cantilever onto an array of photodiodes, and a surface topographical map is generated from which surface roughness values can be calculated schematically, as shown in Figure 13263.

If the tip is scanned at a constant height, a risk would exist that the tip collides with the surface, causing damage. Hence, in most cases a feedback mechanism is employed to adjust the tip-to-sample distance to maintain a constant force between the tip and the sample.

An investigation into the buckling of the surface of the PDMS films with metal ion implantation was done on Co and Fe exposed films at 60 s, 120 s, and 180 s exposure. Various scans of the sine-like undulations and surface cracks were collected. As well, a further series of scans were collected of the coherent and semi-coherent buckling patterns for the Fe exposed films with 10 s and 1200 s exposure times.
2.3.2 Spectroscopic Surface Characterisation Techniques

2.3.2.1 Rutherford Backscattering Spectrometry (RBS)

Rutherford backscattering spectrometry (RBS) is an analytical technique used to determine the structure and composition of materials by measuring the backscattering of a beam of high energy ions striking a sample. RBS utilizes three key elements, an ion source, typically alpha particles, although heavier ions may be used, as He\(^+\) ions were used in this work, a way to accelerate them, with either a single or a double stage system used, depending on the required energy, and a detector capable of measuring the energies of backscattered ions over some range of angles.

For energies greater than 1 MeV, two-stage systems, or "tandem accelerators", are used. Starting with a source of He\(^-\) ions and positioning the positive terminal at the center of the acceleration tube, a stripper element included in the positive terminal then removes electrons from ions, which pass through, converting He\(^-\) ions to He\(^{++}\) ions. The ions start out being attracted to the terminal, pass through and become positive, and are repelled until they exit the tube at ground.

It should be noted, however, that the energy above refers to the product of the accelerating potential and the charge state of the energized ion, and as seen above, the charge state can be +1, +2, +3, +4, or more depending on the atom being accelerated. So a 1MeV single stage machine can yield a range of energies, depending on the accelerating potential and charge.

Commonly, detectors used to measure backscattered energy are silicon surface barrier detectors. These consist of a p-n junction created by coating a very thin layer of p-type silicon on an n-type substrate. Ions which reach the detector lose
some of their energy to inelastic scattering from the electrons, and some of these electrons gain enough energy to overcome the band gap between the semiconductor valence and conduction bands. This means that each ion incident on the detector will produce some number of electron-hole pairs, which is dependent on the energy of the ion. These pairs can be detected by applying a voltage across the detector and measuring the current, providing an effective measurement of the ion energy.

RBS has been used to probe the interfacial structure of calcium phosphate (CaP) coatings on polyethylene (PE) and polydimethylsiloxane (PDMS), for both untreated and oxygen plasma pretreated polymeric substrates \(^{264}\), and also for determining the elemental composition of PDMS hybrid gels prepared via \(^{60}\)Co irradiation \(^{265}\).

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\(\alpha = \) incident angle
\(\beta = \) exit angle
\(\theta = \) scattering angle

**Figure 14:** Schematic of RBS used in this work.
As can be seen in Fig 14, the charge carried by ions impinging on the sample is converted to current, also called the target current (nA), which is then converted to pulses by a current-to-frequency converter (C/F converter). These pulses trigger another pulse, produced by the pulse generator (Pulsar), and the number of these new pulses is proportional to the target current.

On the other hand, the scattered ions which enter the energy detector produce electron-hole pairs. These are separated in an electric field (bias) and come out of the energy detector as charge pulses, which are fed into the charge sensitive pre-amplifier, together with the output of the Pulsar, and after passing through an amplifying stage, the mixed signal (energy signal and Pulsar output) is energy-analysed by a multi-channel analyser (MCA), separated into energy bins and displayed on the PC as the energy spectrum.

As part of the investigation of ion implantation of metal ions into PDMS films, RBS was conducted on all samples, as well as the Si reference samples created for Co and Fe implanted films at 60 s, 12 s, and 180 s exposure times.

2.3.2.2 Elastic Recoil Detection Analysis (ERDA)

Elastic Recoil Detection Analysis (ERDA) is a nuclear technique used to obtain elemental concentration depth profiles in thin films. Just like RBS, an energetic ion beam is directed at the sample to be depth profiled with a kinetic energy exchange between the atoms of the sample and the energetic ion beam used to determine this information. The incident energetic ions typically have energies in the MeV range, enough to kick out the atoms being struck for detection. This presents the greatest advantage of ERDA, as a complete analysis of the sample is immediately available. While RBS uses backscattered projectiles from the atoms in the sample, which are heavier than the incident ions, and then measures the energies of the
backscattered projectiles, ERDA measures the energies of the forward recoil of all atoms in the sample lighter than the incident ions.

ERDA is also often done using a relatively low energy 2 MeV He beam to depth profile hydrogen. Multiple detectors are then used at backscattering angles to detect heavier elements by RBS, along with a forward detector to simultaneously detect the recoiled hydrogen. The recoil detector has to have a "range foil": a thin film to preferentially stop the incident He beam that is scattered into the forward direction.

While RBS has its advantages including: being quantitative without the need for reference samples; non-destructive (although in the case of polymers, this is not entirely accurate); has a good depth resolution of the order of several nm and a very good sensitivity to heavy elements of the order of parts-per-million (ppm), along with an analysing depth of 2-20 µm, depending on the incident ions, it does have a distinct disadvantage when it comes to profiling the change in complex chemistries of modified polymers.

RBS has poor sensitivity in detecting light elements such as C, O and it cannot detect hydrogen, especially in the presence of a substrate of higher mass such as Si, which is the case in this work. This is due to the low Rutherford scattering cross-section, which is proportional to the product of the atomic numbers of the projectile and the scatterer.

To overcome these problems, ERDA is used, which has the advantages of: large recoil cross-sections with heavy ions and hence good sensitivity; almost the same recoil cross-section for a wide mass range of target atoms; and element depth profiling of a wide range of elements from hydrogen to rare earth elements.
ERDA has been used for a direct measurement of hydrogen in highly ordered pyrolytic graphite (HOPG) with minimal disruption of the carbon lattice, as well as determining the hydrogen content of hydrogenated and structurally disordered silicon carbide films, a-SiC:H, with changing deposition parameters.

2.3.2.3 X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) is a quantitative spectroscopic technique that measures the elemental composition, empirical formula, chemical state, and electronic state of the elements that exist within a material, under ultra-high vacuum (UHV) conditions. XPS spectra are obtained by irradiating a material with a beam of X-rays, while simultaneously measuring the kinetic energy and number of electrons that escape from the top 1 to 10 nm of the material being analyzed. It should be obvious that since XPS analysis is limited to the top few nanometers of the surface, even minor surface contamination is pronounced in the results.

Because the energy of a particular X-ray wavelength is known, the electron binding energy of each of the emitted electrons can be determined by using an equation that is based on the work of Ernest Rutherford, and then compared to known values to identify the element and its oxidation state (Eq1):

\[ E_{\text{binding}} = E_{\text{photon}} - (E_{\text{kinetic}} + \phi) \]

Equation 1

where \( E_{\text{binding}} \) is the binding energy (BE) of the electron, \( E_{\text{photon}} \) is the energy of the X-ray photons being used, \( E_{\text{kinetic}} \) is the kinetic energy of the electron as measured by the instrument, and \( \phi \) is the work function of the spectrometer. The resulting spectrum is a plot of arbitrary units of intensity versus binding energy (eV). The intensity of the ejected photoelectrons relates directly to the material surface.
atomic distribution and can therefore be used to quantify percent atomic composition and stoichiometric ratios\textsuperscript{269}.

X-rays are generated by bombarding an anode material with high energy electrons, emitted from a thermal source. The choice of anode material for the XPS technique will determine the energy of the X-ray transition generated, with the most popular choices being Al K\textalpha{} and Mg K\textalpha{}, providing photons of 148636 eV and 1253.6 eV, respectively. Al K\textalpha{} was used in this case. Analysis is done with the use of a Hemispherical Analyser (HSA), consisting of a pair of concentric electrodes, between which there is a gap for electrons ejected from the sample to pass through. Using a potential difference across the two hemispheres, where the outer hemisphere is more negatively charged than the inner, electrons with different energies are separated out and detected using a multi-channel analyser according the equation, $E = k \ e \ \Delta V$ where $k$ is the spectrometer constant and dependent upon the design of the analyser.

The output is graphically mapped to a spectrum of binding energy vs. counts per second in CasaXPS (Figure 15) and can be interpreted from the peak locations along with the peak widths and areas.
Figure 15: XPS spectrum of a PDMS thick film implanted with Au ions (20 min exposure)

When modifying surfaces, XPS is useful for probing the presence of specific functional groups on the surface. For example, Kingshott et al. derivatized hydroxyl and carboxylic acid groups of oxidized PET with trifluoroacetic acid and pentafluorophenol, respectively, and analyzed the resulting fluorine to carbon (F/C) ratios to better understand the nature of the surface functional groups.²⁷⁰

Here, we have investigated the surfaces of Au, Ta, Fe, and Mg implanted PDMS thick films using an exposure time of 1200 s, as well as Mg exposure of 30 s and Au exposure of 5 s. The films were uncoated, and the peak positions and elemental compositions were evaluated and compared to the pristine, unmodified PDMS thick film.
2.3.2.4 RAMAN Spectroscopy

Raman spectroscopy is a spectroscopic technique used to study vibrational, rotational, and other low-frequency modes in a system. Monochromatic light, usually from a laser in the visible, near infrared, or near ultraviolet range is used to illuminate a system. The laser light interacts with phonons or other excitations in the system, resulting in the energy of some of the laser photons being shifted up or down (Fig. 16). The shift in energy gives information about the phonon modes in the system.

When a sample is illuminated with a laser beam, light from the illuminated spot is collected with a lens and sent through a monochromator. Wavelengths close to the laser line, due to elastic Rayleigh scattering, are filtered out while the rest of the collected light is dispersed onto a detector.

Spontaneous Raman scattering is typically very weak, and as a result, the main difficulty of Raman spectroscopy is separating the weak in-elastically scattered light from the intense Rayleigh scattered laser light. For this reason, modern instrumentation almost universally employs notch or edge filters for laser rejection and spectrographs (either axial transmissive (AT), Czerny-Turner (CT) monochromator, or Fourier transform (FT) spectroscopy based) and charge coupled device (CCD) detectors.
Raman spectrometry has traditionally been used to probe the influence of cross-linker concentration on polymer properties\textsuperscript{271} and optical characteristics\textsuperscript{272}, as well as the influence of fillers\textsuperscript{273}. For this study into the surface modification of PDMS thick films with ion implantation, Raman spectroscopy provides a good bulk characterisation tool for the chemistry of the unmodified elastomer film on a silicon supporting wafer. However, due to the transparency of PDMS to the wavelength of light used and the thin volume of surface modifications compared to the unmodified bulk elastomer film, Raman spectroscopy is not a relevant technique for probing the changes to the surface. Multiple scans comparing the pristine film to different Fe exposure times confirm this.

### 2.3.2.5 Ultraviolet-Visible Spectroscopy (UV-Vis)

Ultraviolet-visible spectroscopy (UV-Vis) refers to absorption spectroscopy in the UV-visible spectral region. The absorption in the visible range directly affects the
perceived colour of the chemicals involved since different molecules absorb radiation of different wavelengths. An absorption spectrum will show a number of absorption bands corresponding to structural groups within the molecule. In this region of the electromagnetic spectrum, molecules undergo electronic transitions, that is, transitions involving $p$, $s$, and $n$ electrons; transitions involving charge-transfer electrons; or transitions involving $d$ and $f$ electrons.

When an atom or molecule absorbs energy, electrons are promoted from their ground state to an excited state. In a molecule, the atoms can rotate and vibrate with respect to each other. These vibrations and rotations also have discrete energy levels, which can be considered as being packed on top of each electronic level.

Absorption of ultraviolet and visible radiation in organic molecules is restricted to certain functional groups (chromophores) that contain valence electrons of low excitation energy. The spectrum of a molecule containing these chromophores is complex. This is because the superposition of rotational and vibrational transitions on the electronic transitions gives a combination of overlapping lines. This appears as a continuous absorption band.

While there are a variety of possible electronic excitations that may occur in organic molecules, such as $\text{CH}_3$, as shown in Fig. 17, only the two lowest energy ones are achieved by the energies available in the 200 to 800 nm spectrum.
For this study into the surface modification of PDMS thick films with ion implantation, UV-Vis provides a good bulk characterisation tool for the chemistry of the unmodified elastomer film on a silicon supporting wafer. Due to the thin volume of surface modifications compared to the unmodified bulk elastomer the information this technique can provide is limited. However unlike Raman techniques, it is measuring absorbance of the film, which is expected to change with increased exposure. Multiple scans comparing the pristine film to different Fe exposure times confirm this.

2.3.3 Other Surface Characterisation Techniques

2.3.3.1 X-ray Diffraction (XRD)

X-ray diffraction (XRD) is a commonly used, non-destructive technique and although this is not strictly true for polymers, decreasing the energy and angle of the beam limits the damage and still yields important information. XRD reveals detailed information about the chemical composition and crystallographic structure of natural and manufactured materials. When a monochromatic X-ray beam with wavelength \( \lambda \) is projected onto a crystalline material at an angle \( \theta \),
diffraction occurs only when the distance travelled by the rays reflected from successive planes differs by a complete number $n$ of wavelengths. By varying the angle $\theta$, the Bragg's Law conditions are satisfied by different $d$-spacings in polycrystalline materials (Fig. 18). Plotting the angular positions and intensities of the resultant diffracted peaks of radiation produces a pattern, which is characteristic of the sample. Where a mixture of different phases is present, the resultant diffractogram is formed by addition of the individual patterns.

![Bragg's Law Schematic](image)

**Figure 18**: Schematic illustrating Bragg’s Law.

When conducted on polymeric materials, however, XRD does not produce sharp intense spectra as in other crystalline materials. This is because polymers are semicrystalline, containing a crystalline portion and an amorphous portion. The crystallite size in polymers is usually on the nanoscale in the thickness direction, and due to the long chains and low density of polymers, highly susceptible to orientation.

Glancing angle is an XRD technique where the incident angle is locked at a low angle so as to ensure that information gathered is only from uppermost layers in the sample. This allows for a degree of depth profiling as the incident angle is locked at progressively greater angles, and successive diffraction patterns are
collected. Potential changes in the crystallinity and in micro- and macro-strains as a result of ion implantation within the elastomer surface are of particular interest.

Both $\theta$-2$\theta$ scans, as well as glancing angle scans, were conducted on the Ni, Ni/Fe, Ni/Eu, Si, and Co 900 s implanted films. The crystallographic and compositional changes were probed, along with stress-related peak shifts in the surface layers as a result of implanting different metal ions species, as well as mixtures of them.

### 2.3.3.3 Contact Angle

Water contact angle measurements can determine surface hydrophilicity by measuring the angle at which a liquid/vapor interface meets a solid surface. The lower the contact angle, the more hydrophilic the surface is.

![Figure 19: Schematic of contact angle calculations.](image)

The contact angle is described by an equation which links the surface tension between the liquid and the surface ($\gamma_{SL}$), the surface tension between the liquid and the gas environment over the drop ($\gamma_{LG}$), and the surface tension between the gaseous environment and the surface ($\gamma_{SG}$) (Eq 2).

$$\gamma_{SG} = \gamma_{SL} + \gamma_{LG} \cdot \cos \theta$$

*Equation 2*
When the contact angle is high, the surface is hydrophobic, and the interaction between the liquid and the surface is weak. When the contact angle is low and the liquid drop spreads out across the surface, the surface is hydrophilic, and the interaction between the liquid and the surface is strong. The contact angle measurement involves a complex and wide variety of intermolecular interactions that is simplified by the Owens-Wendt-Rabel-Kaelble model\textsuperscript{274}, where the intermolecular interactions are split into polar and dispersic interactions. Based on this split, the contact angle measurements are conducted with two types of liquids, so that the polar and dispersic components of surface energy can be calculated.

The measurements of contact angle were performed with a contact angle goniometer and microscope, and the results were then analysed with software. The wettability of Fe, Mg, Ta, and Au implanted films were recorded at different exposure times and compared to that of the unmodified surface of PDMS. All measurements were taken at a minimum of 48 hours after ion implantation.

For Fe, data for exposure times of 5 s and 1200 s were recorded, for Mg, 1200 s, for Ta exposed films, data for both 30 s and 1200 s were recorded, and for Au exposed surface, data for 10 s, 30 s, and 1200 s were recorded. Fe, Mg, and Ta 1200 s exposed films were then biologically tested with neuroblastoma cellular cultures as described below.

### 2.3.3.4 Biocompatibility Testing – Neuroblastoma Cell Culture

To determine the effectiveness of the surface modification of low energy metal ion implantation of PDMS thick films, the larger pieces of PDMS films, unmodified films and Fe, Mg, and Ta 1200 s exposed films on Si wafer support were broken apart into squares, in pieces large enough to completely include the 4 mm implanted islands in the case of the modified surface, and placed into a 24-well plate, with 6 repetitions for each sample. L929 fibroblast cells were cultured on the native and
modified PDMS substrates. Dulbecco’s Modified Eagle Medium: Nutrient Mixture F-12 (DMEM/F12) supplemented with 20% (v/v) fetal bovine serum (FBS) was used for all experiments. Samples of native and modified PDMS were rinsed with 95% ethanol before placing them face up in the wells of a sterile 24-well plate (Greiner, Sydney) and sterilized by exposing them to UV light in a laminar flow hood for 4 h. Each well was then seeded with 500,000 cells and cultured at 37 °C with 5% (v/v) CO₂ for 48 h before the film inserts were taken out and gently dipped into fresh tissue culture medium to wash off any non-attached cells. Calcein-AM was used to measure cell viability. The washed inserts were next placed into separate wells of a new 24-well plate, and 0.5 ml of DMEM/F12 containing 1 µM calcein-AM (Invitrogen, Sydney) was subsequently added to each well. The entire plate was then incubated for 30 min at 37 °C before representative optical photographs were taken of each sample, and a mean cell count was used to determine normalised cell numbers between samples.

Representative optical microscope and fluorescence images of the modified and unmodified PDMS surfaces taken from samples within different wells were used to create a data mean count of viable cells, which was taken and normalised against the mean cell count for the pristine PDMS surface.
Part 3: Results and Discussion

Chapter 3: An investigation of the pristine, unmodified PDMS thick film

Prior to ion implantation, the PDMS film was inspected and characterised by a number of techniques to ensure its quality and stability over time. A thorough investigation of the surface via scanning electron microscope (SEM), as seen in Figure 20, and atomic force microscope (AFM). Elastic Recoil Detection Analysis (ERDA) and Rutherford Backscattering (RBS), in Figs. 21 and 22, respectively, were used to study the chemical compositions of the films and their relative homogeneity, while the optical techniques, Raman and UV-VIS spectroscopy, were used to further investigate the chemistry of the film as well as its porosity.

The spin-coated PDMS thick films that were used for ion implantation were demonstrated to consistently have a smooth, homogeneous, and featureless aspect (Fig. 20). These features appeared to be stable over time, as evident from inspecting the PDMS film surface over a period of days and weeks.

Figure 20: SEM image of the surface of a PDMS film prior to ion implantation. The square in the middle is a beam focussing contamination spot.
The chemical composition with depth of the unmodified film was also investigated with Elastic Recoil Detection Analysis (ERDA), carried out on ANSTO’s STAR accelerator (2MV HVEE Tandem accelerator) with 1.8 MeV He\(^+\) ions; the results were analysed with SIMNRA code, as seen in Fig. 21.

Figure 21: SIMNRA analysis of ERDA on an unmodified PDMS thick film on a silicon support wafer.

The results for the unmodified PDMS thick film were compared with those from Kapton (H = 25.64at%; C = 56.41at%; N = 5.13at%; O = 12.82at%), which is known to be a stable polymer under ion beam bombardment. The above fit was achieved for a PDMS film composition of H = 42at%; C = 20at%; Si = 28at%; O = 10at%. This was a little different from the expected PDMS formula SiC\(_2\)H\(_6\)O, with a composition of H = 60at%; C = 20at%; Si = 10at%; O = 10at%; and a density of 0.97g/cm\(^3\). The smaller amount of H and larger amount of Si suggest that the PDMS polymer coating was not uniform in thickness, composition, or coverage of the Si substrate – although
from a visual inspection and the previous SEM and AFM study, a non-uniform composition seems more likely.

Furthermore, Rutherford Backscattering (RBS) analysis was performed on the unmodified PDMS thick film (Fig. 22) on a supporting Si wafer to obtain information on the relative concentrations of its constituent elements and to investigate the distribution of these elements in depth to determine its compositional homogeneity. In the RBS spectrum, the channel number associated with the edge identifies the element. The flat shape of the step between edges indicates the uniformity of the distribution of that element inside the 3 \( \mu \text{m} \) surface layer of the thick film that is probed by the technique. The difference in yield between horizontal steps indicates the relative concentrations of the elements in the material.

Figure 22 shows layers with varying composition within the thick elastomer film, demonstrating the non-uniform composition of the elastomer film. It is expected that this is a result of remnants of uncured raw materials in the PDMS thick film, a supposition supported by subsequent Raman scans. It is well known that too much of these raw materials in the cured polymer matrix affects the thermal and mechanical properties of the film. Since most work in the literature with PDMS elastomer is within the bulk regime with thicknesses greater than 200 \( \mu \text{m} \), and due to the high mobility of the polymer chains, the literature does not place much value on optimizing the mixing of and curing conditions of the liquid PDMS. However, as seen for films on the order of 4 \( \mu \text{m} \) thick, it may play an important role in further refining the buckling and surface modification process. Mixing optimization of the catalyst and base becomes of particular interest if the mechanical strength of the film is critical for the scientific and technological application of the buckled system.
Figure 22: RBS spectrum of unmodified PDMS on a Si support wafer. The small Te contamination on the surface of the Si wafer appears to be from process contamination present on the purchased wafers.

RBS found the presence of a small amount of Te in the PDMS film. It is speculated from the higher concentration at the surface with a gradual decrease in concentration towards the interface with the silicon substrate that this is a chemical contamination rather than one present in the silicon or the cathode.

This explanation was reinforced by Raman spectrometry, as shown in Fig. 24, which indicates that elements of the raw material silane and vinyl groups survive the curing process. Table 5 gives a summation of the displayed bands along with the assigned values. A laser with a wavelength of 785nm was used with the spot covering several buckles, as seen in Figure 23. The Raman results were duplicated in several areas of the film, including over several large surface cracks, and any variance was with the margin of error for the equipment. This is to be expected, since PDMS is known to be optically transparent down to 300 nm, and as such, the largest peak comes from the Si support wafer. Also, while Raman spectroscopy was conducted for a range of exposure times to ion implantation, any change of the
surface volume was disguised by the bulk volume of unmodified PDMS in the thick film, so only the scan of the pristine film is shown (Fig. 24).

Figure 23: Raman laser spot on metal ion implanted PDMS thin film.

The Raman spectrum shows the fingerprint of PDMS peaks for –Si-O- symmetrical stretching at 480 cm\(^{-1}\), –C-Si- symmetrical stretching at 515 cm\(^{-1}\), -C–Si-C- symmetrical stretching at 710 cm\(^{-1}\), -C-H symmetrical bending at 1264 cm\(^{-1}\), and lines at 2906 cm\(^{-1}\) and 2971 cm\(^{-1}\) corresponding to the CH\(_3\) side chains, specifically the –C-H symmetrical stretching. There are strong peaks at 940 cm\(^{-1}\) and 1410 cm\(^{-1}\) that correspond to plane angular deformations and vibrations of un-cured vinyl groups.

The two peaks shown at 2907 and 2971 cm\(^{-1}\) assigned to the CH\(_3\) groups were expected to decrease with increased ion implantation, and the destruction of the original silicone structures, such as CH\(_3\), Si–CH\(_2\), and Si–CH\(_3\), and the formation of new functional groups such as OH and CO were expected to be reflected in the Raman spectra. However, as previously explained, these changes occurred only at the surface and were obscured by the large signals obtained from the bulk unmodified PDMS thick film and the Si support wafer.
Figure 24: Raman spectrum of unmodified PDMS on a silicon support wafer.

Table 6: Variational spectra of the PDMS (cured at 80°C, mix 1:20) thick film.

<table>
<thead>
<tr>
<th>Raman spectrum</th>
<th>Wavenumber (1/cm)</th>
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<tr>
<td></td>
<td>303</td>
<td>SiC$_2$ wag</td>
</tr>
<tr>
<td></td>
<td>480</td>
<td>Si-O symmetrical stretching</td>
</tr>
<tr>
<td></td>
<td>515</td>
<td>– C-Si- symmetric stretching</td>
</tr>
<tr>
<td></td>
<td>710</td>
<td>-C–Si-C- symmetric stretching</td>
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<tr>
<td></td>
<td>791</td>
<td>-C-Si- symmetric stretching</td>
</tr>
<tr>
<td></td>
<td>857</td>
<td>CH$_3$ rocking</td>
</tr>
<tr>
<td></td>
<td>940</td>
<td>–CH$_3$ - rocking mode for vinyl silanes</td>
</tr>
<tr>
<td></td>
<td>1264</td>
<td>C-H symmetrical bending</td>
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<tr>
<td></td>
<td>1410</td>
<td>C-H vibrations in the vinyl group</td>
</tr>
<tr>
<td></td>
<td>2906</td>
<td>C-H sym stretching</td>
</tr>
<tr>
<td></td>
<td>2971</td>
<td>C-H sym stretching</td>
</tr>
<tr>
<td></td>
<td>3061</td>
<td>– C-H asymmetric stretching $T_2$ mode of methane</td>
</tr>
</tbody>
</table>
Further evidence of the non-uniform composition of the polymer matrix comes from the UV-VIS investigation of both the unmodified PDMS thick film and ion implanted films with a gradual increase in exposure time, as shown in Fig. 25. Also, more success was achieved at detecting modifications with increased dose using this optical technique as opposed to Raman spectroscopy. The relative reflectance was measured at an 8° incident angle over a wavelength range from 400 – 800 nm with a halogen bulb. The vertical scale of the data is absorbance. The unmodified films show a non-homogeneous curve that is synonymous with variations in porosity or non-uniform composition. As the exposure to energetic ions is increased and the surface oxidatively decomposes to a homogeneous silica-like layer, the absorbance decreases and the absorbance peak ‘smoothes out’.

\[ \text{Absorbance (Instrument Units)} \]

\[ \text{Wavelength (nm)} \]

Pure PDMS
Pure PDMS + 1 Sec of Fe Implantation
Pure PDMS + 5 Sec of Fe Implantation
Pure PDMS + 10 Sec of Fe Implantation
Pure PDMS + 20 Sec of Fe Implantation
Pure PDMS + 120 Sec of Fe Implantation
Pure PDMS + 180 Sec of Fe Implantation

Figure 25: UV-VIS spectrum of unmodified PDMS thick film on Si support wafer compared to spectra after a variety of doses of Fe ion implantation.

In good agreement with the literature, it has been found that Poly-(dimethylsiloxane), a commonly used, silicon-based, organic, cross-linkable elastomer, is homogeneous, isotropic, and optically transparent down to 300 nm. In its cross-linked state, the elastomer does not permanently deform under stress or strain, and it is stable over a wide temperature range. PDMS is chemically inert,
and so the material can be made biocompatible with appropriate chemical and/or physical treatment to enable it to give the desired interfacial interactions. These properties make PDMS desirable for use in the production of numerous active and passive implantation devices that are in direct and sometimes prolonged contact with human tissues, from artificial lungs to artificial finger joints.
Chapter 4: Low Energy Metal Ion Implantation into PDMS

4.1 Physical Consequences of Metal Ion Implantation of PDMS Thick Films: Investigation of the Onset and Evolution of Buckling

Immediately after the metal ion implantation was carried out, the surface of the polymer irradiated by the ion flux becomes altered and covered by what appears to be stress-induced V-shaped cracks that penetrate deeply into the elastomer matrix (Fig. 26). It is well known and has been demonstrated that V-shaped cracks tend to open up on the surface as a method of strain relief, and thus, as expected, the frequency of these V-shaped cracks increases with implantation dose. This is a result of the decomposition of the surface into a fragile thin silica-like layer, which cracks due to compressive stress. The process of oxidative decomposition is detailed later. As also detailed later, some metal ion species induce greater strain into the elastomer matrix than others, increasing the frequency of occurrence for V-shaped pits.

Figure 26: Optical photographs of cracks on the surface of ion implanted PDMS films: (a) 20 min Ti implanted, (b) 20 min Ta implanted.

Figure 27 shows an AFM scan, including cross-sectional analysis of a V-shaped crack, with the strain relief induced V-shaped crack being approximately 2 μm in
depth, penetrating deeply into the elastomer matrix. Figure 28 shows a smaller surface crack resulting from stress relief following a 180 s Co ion implantation of the PDMS surface, demonstrating that there are varying surface crack depths coexisting in the surface.

![Section Analysis](image)

![AFM scan](image)

Figure 27: Typical AFM scan of a characteristic heat induced surface crack. Note the V shape, indicating a strain-induced feature.

The strain relief cracks were, in fact, far deeper than the penetration depth of the metal ions or even the depth of the chemical modification of the polymer as a result of other atomic processes, as detailed later in the chapter. It was found that increasing the surface damage through increased dose and/or the use of heavier ions increased the pit depth and frequency, although, as can be seen, different depth cracks can and do coexist on the surface.
Figure 28: AFM images of small surface crack associated with 3 min Co exposure of PDMS thick film supported on a Si wafer: (a) top view, and (b) 3D projection.

Over time, a wave-like regular pattern, evident in the SEM image in Fig. 29 and the AFM scan in Fig. 30, completely covers the surface of the film, filling in the space between the surface cracks. The time required for the regular buckling pattern to appear was governed by the implanted metal ion species and ranged from nearly instantaneous to several hours. This represents a new mechanism for creating and controlling buckling on the surface of PDMS.

Figure 29: (a) SEM image of Ni + Eu implanted PDMS thick film; (b) back-scattered SEM image of Ni + Eu implanted PDMS thick film.

It was thus recognised that the implantation of metals into the surface of PDMS, past a critical dose, served to deliver results comparable to those observed by Bowden et al\textsuperscript{186}. Due to its proven stability and original unstrained and homogeneous features, this behaviour would not spontaneously occur without
modification of the PDMS surface. TEM results detailed later show that the elastomer matrix remains well adhered to the silicon support wafer and the modified silica-like surface layer.

Figure 30: Sectional AFM scan of the characteristic sine-function-like ripples. Different metal ion species result in altered frequency and amplitude of buckles. In this case, the amplitude is 1.025 µm and wavelength and 5.664 µm.

In good agreement with the literature and general buckling theory, it can be seen in Figure 31 that for an increase in Co ion implantation of the PDMS surface, a corresponding increase in amplitude also occurs. This result was replicated with Fe ion implantation as well.
AFM of the buckled PDMS surface reinforced the good adhesion that silicon rubber is known for. As the surfaces aged and were handled, the surfaces of the buckles picked up dust particles and other sources of debris contamination, which was a common feature of AFM scans. Figure 32 shows both contact mode and friction mode of a buckled region for 10 s Fe ion implanted PDMS thick films.

We have already clearly demonstrated that the PDMS film is homogeneous and stable over a time period of weeks, with the buckling of the surface not spontaneously appearing without external stimuli. AFM was conducted in contact mode on partially covered films (Fig. 33), demonstrating the clear transition between the implanted and non-implanted surface behaviour. The covered film remained smooth, homogeneous, and optically transparent, as expected, while the
exposed region of the film showed damage to the PDMS surface in the form of large V-shaped cracks and buckling, as seen in Figure 33 in an AFM sectional scan. Both the surface and the cross-sectional analysis are displayed.

Figure 33: AFM scan of the interface between the unmodified film and the metal ion implanted film. The film was partially covered with a piece of Al foil.

Visible undulations appear even for relatively short periods of exposure of seconds to tens of seconds, with the critical dose dictated by which metal species is being implanted. This characteristic buckling that dominates the surface, from the cross-sectional analysis appears to be remarkably sine-wave-like. The amplitude of these exposures are just over 1 micron in size. The amplitude and frequency of these features can be controlled through the accelerating voltage, fluence, and current of
the ion beam or the metal ions species. It is proposed that altering these parameters affects the thickness of the stiff film by altering the penetration depth of the metal ions\textsuperscript{52, 224}. The AFM and optical microscopy showed similar sine-like buckling behaviour in all films, independent of the ion species implanted. What differed was the amplitude and frequency of the surface ripples, and the depth and frequency of the stress induced cracks, which were influenced by the dose of the implanted metal ion.

![Image](image.png)

Figure 34: Complex buckling pattern around a surface crack for 15 min Fe ion implanted PDMS film on a supporting Si Wafer.

In fact, the interaction between surface cracks and the wave-like regular patterns that fill the spaces between the cracks and edges over time is itself proof that what is occurring is a strain relief phenomenon (Fig 34). The right angles and length of parallel buckling immediately at the edge of the buckles is a demonstration of specific strain minimisation effects. Figs. 35 and 36 demonstrate the complex strain minimisation effects where there is an intersection of two or more surface cracks. Regions of semi-coherent, coherent, and non-buckled areas are created, which
leads to the possibility of controlling buckling regimes, an investigation which is detailed in later chapters.

Figure 35: Complex buckling pattern around the intersection of several surface cracks for 15 min Ni ion implanted PDMS film on a supporting Si wafer.
Figure 36: Complex buckling pattern around the intersection of two surface cracks for 15min Ni ion implanted PDMS film on a supporting Si wafer.

To track the evolution of the buckling process with increasing dose in greater detail, films were exposed to very small doses, which were gradually increased (Fig. 37). As the implantation doses increased, the frequency of the V-shaped cracks, the wavelength of the buckles, and the density of buckling increased until reaching a saturation point, after which no further increase in buckling density was seen.

Figure 37: The evolution of buckling effect with dose: a) with 5 s of Fe implantation, b) 25 s of Fe implantation, c) 3 min of Fe implantation. White area outside buckling is the unmodified film.
It was mentioned earlier that immediately after ion implantation, surface cracks appear, but the buckling appears over time. The buckling is initiated from V-shaped cracks, defects, voids, dust particles, and even edges on the surface, quickly branching out to completely cover the surface of the exposed films in a semi-chaotic pattern of herringbone ripples. Even damage done to the homogeneous surface as a result of the ion implantation process can result in an initiation site, and at higher doses, a method for controlling the buckling regime. It was noticed that the time required for these complex, coherent, and semi-coherent buckling domain patterns to appear was governed by the implanted metal ion species and the time of exposure. The exposure time required to generate these patterns ranged from nearly instantaneous to a period of several hours.
To further investigate the surface buckling process at higher doses and over wider areas, optical microscopy was used to examine the PDMS film surface, and the result is shown in Figure 40. Because buckling is also a stress related phenomenon and any stress is relieved at the V-shaped cracks on the surface, any buckling becomes ordered perpendicular to these cracks. Away from the V-shaped cracks, the buckling becomes disordered and forms a multitude of partial domains.
Figure 40: Optical image of both ordered and disordered buckling on the surface of the ion implanted PDMS. Partial domain structures are clearly visible away from the surface cracks. Inset: Lower magnification image of the film, showing the transition between the covered non-modified area and the modified surface.

Higher doses and a combination of ions have a greater or lesser impact on the strain effects, and this is demonstrated by the varying buckling regimes, and the wavelength and amplitude of the buckling across the exposed PDMS surface. Figure 41 shows a PDMS film that has been exposed for half an hour: 900 s of both Ni and Eu, respectively.
Figure 41: Complex buckling pattern of 900 s Ni and 900 s Eu ion implanted PDMS film on a supporting Si Wafer

This leaves the surface relatively more fragile leaving it more vulnerable to wear effects, as seen in the bottom of Figure 42, which presents a PDMS film implanted with both Ni and Fe. Even the buckling has assumed a plastic melted look, which implies extreme strain effects on the surface, effects which optical microscopy is ideally suited to picking up.
Figure 42: Complex buckling pattern of 15 min Ni and 15 min Fe ion implanted PDMS film on a supporting Si wafer. Wear is evident in the bottom left from prolonged handling.

Figure 43 is a further demonstration of extreme buckling effects due to strain minimisation and a demonstration of how powerful this technique is for bottom up patterning of the surface. Below, the PDMS film has been Fe ion implanted for 180 s and shows buckling amplitude of 2.6 µm for an approximately 4 µm thick film with ion implantation depth effects only affecting the top 100-200 nm.
Figure 43: AFM of surface buckling for 180 s Fe implanted PDMS film

The different surface domains which result are due to the patterns established by the interference of the differing orientations of the waves that were formed (Fig. 44(a)). These buckling domains completely cover the surface of the film and fill in the space between the surface cracks. A domain boundary was imaged by AFM and is shown in Fig. 44(b), supporting the cross-sectional TEM results in showing no evidence of delamination, simply the intersection of stress wave fronts, which produces an optical illusion of height changes. This becomes useful when designing or controlling discrete strain regions for use in technological and scientific applications, since it means that the stiff layer remains coupled to the underlying elastomer base, thereby retaining the bulk elastomer properties of PDMS.
Figure 44: AFM across the intersection of strain induced buckling patterns: a) optical microscope image showing the region of interest, b) AFM scan across an intersection of strain wave fronts, in this case the corner of a polygon. This result is repeated across all intersections, and there is no evidence of delamination occurring.

Optical images of both Au and Ti implanted films are shown below (Figs. 45, 46) to show the complexity of a variety of intersecting strain minimisation fronts that occur over a large area, as well as the uncontrolled and random nature of buckling without initiating some controls over parameters.

Figure 45: Incoherent buckling pattern of 20 min Au implanted PDMS film on a supporting Si wafer.
Figure 46: Multiple intersecting stress buckling fronts resulting in the appearance of a complex, multiple height bucking pattern in the above 10 min Ti implanted PDMS film on a supporting Si wafer.

It is possible to create large areas of buckling without surface cracks, as well as to control and manipulate the coherent and semi-coherent buckling regimes that come from the specific strain minimisation effects. A detailed investigation of this follows in Chapter 5. This represents a new mechanism for creating and controlling buckling on the surface of PDMS. As can be seen in Figs. 37 and 38, visible undulations appeared on the implanted surface even for relatively short periods of exposure of seconds to tens of seconds, with the critical dose dictated by which metal species is being implanted.
4.2 Chemical Implications of Metal Ions Implanted Into Elastomer Thick Films

A qualitative analysis suggests the cause of the time dependence of wrinkle pattern formation for the metal ions implanted. When an energetic ion impacts the surface of the elastomer, the structure and composition are irreversibly changed, primarily through chain scission into lower molecular weight chains and the release of volatile species, to a depth that depends on the mass of the implanted metal ion and its energy. At the same implantation energy, the more massive an implanted ion is, the less it will penetrate into the material and the narrower the Gaussian profile of implantation will be, due to the way in which the energetic ion loses energy in the solid matrix, mostly through interaction with the electrons of the target. This leads to variations in the depth and thickness of the metal rich layer implanted into the polymer matrix, as well as the decomposed silica-like layer on the surface of the elastomer bulk.

Take Ni as an example: Ni is produced in 3 charge states, +1, +2, and +3, with each charge state having a probability of 24.5%, 74.7%, and 0.77% respectively. This results in 3 separate acceleration voltages during the same implantation process, 45 keV, 90 keV, and 135 keV, which, in turn, implies different ion implantation doses, as shown via SRIM calculation in Figure 47.

Figure 47: Accelerated ion ranges for 45 keV Ni into a PDMS thick film calculated by SRIM: (a) Q = +1, 45 keV, (b) Q = +2, 90 keV, (c) Q= +3, 135 keV.
Also, as discussed earlier, again using Ni as an example, the penetration depth of Ni ions (red) into PDMS triggers collision cascades with H (green), C (blue), O (magenta), and Si (light blue) atoms of the polymer. This depth distribution creates a teardrop like feature of atomic interactions beneath the surface, which again differs according to charge state and accelerating voltage, as shown below in Figure 48.

Figure 48: Collision cascade as a result of 45 keV Ni ions implanted into a PDMS thick film calculated by SRIM: (a) Q = +1, 45 keV, (b) Q = +2, 90 keV, (c) Q = +3, 135 keV.

Similar effects are seen for all metal ions used, making allowances for the ion mass and charge. What results are changes in the surface chemistry, as well as a deposited metal rich volume as a result of the ion implantation process. Extensive SRIM calculations have been done on both Fe and Co implanted films that show the variations in atomic compositions with depth. Cross-sectional TEM and XPS follow later due to the inaccuracy of RBS when used for detecting lighter elements. However, it does confirm the presence of a metal volume within the PDMS films, as well as the changing chemistry as a result of the implantation process.

As mentioned earlier RBS was conducted on a variety of metal ion implanted PDMS films at a variety of doses to detail the effects of implantation, as well to confirm that a metal volume was successfully implanted inside the film. Note that in the RBS spectrum, the channel number associated with the edge identifies the element, while the shape of the step between edges infers the uniformity or otherwise of the distribution of that element inside the material that is probed by the technique. The difference in yield between horizontal steps gives an indication of the relative atomic concentrations within the material. As expected, C, Si, O, and the relevant
metal ions were all present, although the elemental concentrations were not homogeneous throughout the elastomeric film.

The following RBS scans, Figure 49 for Co implanted PDMS films and Figure 50 for Fe implanted PDMS films, respectively, detail clearly that this was the case, as well as clearly demonstrating, despite the issues that may exist in using RBS for the detection of lighter elements, the increase in the silicate layer at the surface due to thermal degradation. Tables of the SIMNRA simulation follow the RBS spectra (Tables 7 and 8, respectively).

Figure 49: RBS spectra of 45 keV Co implantation into a PDMS thick film with exposure of a) 60 s, b) 120 s, c) 180 s, d) 900 s.

Excepting variations in atomic composition with depth, a phenomenon that appears quite clearly in the cross-sectional TEM discussed later, as the surface PDMS decomposes into a silicate-like structure, an increase in Si and decrease in H is
witnessed. At higher doses, the C concentration starts to increase, evidence of oxidative burning, as reflected in the SIMNRA simulation.

Table 7: SIMNRA simulation of the atomic composition of PDMS with depth due to Co ion implantation.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Si [at%]</th>
<th>H [at%]</th>
<th>C [at%]</th>
<th>O [at%]</th>
<th>Te [at%]</th>
<th>Co [at%]</th>
<th>Thickness [ML]</th>
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<tr>
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<td>42.0</td>
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<tr>
<td>4</td>
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<tr>
<th>Layer</th>
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<th>H [at%]</th>
<th>C [at%]</th>
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</table>

In the case of Fe implanted PDMS films, as in the Co implanted films, there is an inhomogeneity in the atomic compositions. This was apparent even in the
unmodified film in Fig. 22, although this inhomogeneity seems to have been exacerbated by the ion implantation process, as expected by nature of the ion-PDMS interactions, as well as the thermal decomposition of the polymer.

![RBS spectra](image)

Figure 50: RBS spectra of 45 keV Fe implantation into a PDMS thick film for a) 60 s, b) 120 s, c) 180 s, d) 900 s.

As mentioned earlier, the Te contamination shown in the RBS spectra appears to be a chemical contamination in the PDMS due to the positioning of the Te in the graph. This low concentration of Te contamination is not expected to significantly affect the results, and it is not apparent in all samples, so does not seem to be a systematic problem.

More broadly, the very distinctive Gaussian peaks representing the metal volume within the PDMS polymer matrix are a good indication of the homogeneity of the
depth distribution of the implanted metal ions. The thickness of these Gaussian peaks gives the thickness of the implanted metal volume. Where ion implantation has been combined, as in Figure 51, where Co and Eu were implanted into a PDMS thick film, there is greater evidence of oxidative burning, with complex carbon and oxygen compounds evident on the surface. The strain effects of combining elements are investigated in more detail later with glancing angle XRD.

Figure 51: RBS spectrum showing results of Co implantation of PDMS film for 900 s followed by Eu implantation for 900 s.

Table 8: SIMNRA simulation of the atomic composition of Co and Eu ion implanted PDMS film. Each Ion was implanted for 900 s.

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<td>400</td>
</tr>
<tr>
<td>4</td>
<td>45.0</td>
<td>41.0</td>
<td>6.9</td>
<td>7.1</td>
<td></td>
<td></td>
<td>5,200</td>
</tr>
<tr>
<td>5</td>
<td>100</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Bulk Si</td>
</tr>
</tbody>
</table>
Table 9: SIMNRA simulation of the atomic composition of PDMS with depth due to Co ion implantation.

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<thead>
<tr>
<th>Layer</th>
<th>Si [at%]</th>
<th>H [at%]</th>
<th>C [at%]</th>
<th>O [at%]</th>
<th>Fe [at%]</th>
<th>Thickness [ML]</th>
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<tbody>
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<td>60s Fe</td>
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<tr>
<td>1</td>
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<td>630</td>
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<tr>
<td>2</td>
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<td>30.0</td>
<td>27.8</td>
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<tr>
<td>3</td>
<td>40.0</td>
<td>41.0</td>
<td>13.9</td>
<td>5.1</td>
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<td>5,000</td>
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<td>100</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Bulk Si</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Layer</th>
<th>Si [at%]</th>
<th>H [at%]</th>
<th>C [at%]</th>
<th>O [at%]</th>
<th>Fe [at%]</th>
<th>Thickness [ML]</th>
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<tbody>
<tr>
<td>120s Fe</td>
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<td></td>
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<td>0.1</td>
<td>800</td>
</tr>
<tr>
<td>3</td>
<td>40.0</td>
<td>41.0</td>
<td>13.9</td>
<td>5.1</td>
<td></td>
<td>5,000</td>
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<tr>
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<td>100</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Bulk Si</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>Layer</th>
<th>Si [at%]</th>
<th>H [at%]</th>
<th>C [at%]</th>
<th>O [at%]</th>
<th>Fe [at%]</th>
<th>Thickness [ML]</th>
</tr>
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<tbody>
<tr>
<td>180s Fe</td>
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<td></td>
</tr>
<tr>
<td>1</td>
<td>65.0</td>
<td>15.2</td>
<td>7.0</td>
<td>8.0</td>
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<td>27.8</td>
<td>2.1</td>
<td>0.1</td>
<td>850</td>
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<tr>
<td>3</td>
<td>40.0</td>
<td>41.0</td>
<td>13.9</td>
<td>7.1</td>
<td></td>
<td>5,000</td>
</tr>
<tr>
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<td>100</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Bulk Si</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Layer</th>
<th>Si [at%]</th>
<th>H [at%]</th>
<th>C [at%]</th>
<th>O [at%]</th>
<th>Fe [at%]</th>
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<tr>
<td>900s Fe</td>
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<td></td>
</tr>
<tr>
<td>1</td>
<td>64.0</td>
<td>7.0</td>
<td>14.0</td>
<td>9.8</td>
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<td>0.2</td>
<td>570</td>
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<td>2</td>
<td>44.0</td>
<td>22.1</td>
<td>30.7</td>
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<td>0.1</td>
<td>850</td>
</tr>
<tr>
<td>3</td>
<td>38.0</td>
<td>41.0</td>
<td>13.9</td>
<td>7.1</td>
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<td>3.0</td>
<td>4,800</td>
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<td>4</td>
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<td></td>
<td></td>
<td></td>
<td>Bulk Si</td>
</tr>
</tbody>
</table>

RBS confirmed the existence of a silicon and oxygen rich layer at the surface of all the ion-implanted film to varying degrees of thickness. The long-range atomic order was also probed with grazing angle XRD in both the silicon rich layer and the elastomer matrix for films implanted with different metal ion species. The results for Ni implanted PDMS are shown in Fig. 52; all metal species and other various combinations of implanted ions displayed similar results. To this end, the surface of
a thick polydimethylsiloxane (PDMS) film was modified with different metal ions and/or a combination using metal ion implantation techniques. X-ray diffraction shows evidence that the implantation process quickly proceeds through chain-scission, with large, highly textured surface crystals of silica appearing at the surface of a stiff silicon and oxygen rich layer adhered to the elastomer base, where the thickness and the concentration of silicon depends on the penetration depth and dose of the implanted ions. As such, controlling the accelerating voltage and fluence or current of the ion beam can further influence the formation of this silicon and oxygen rich film.

Figure 52: Grazing angle XRD of Ni implanted PDMS thick film with exposure of 15 min (~17,000 shots). The increasing angle of incidence shows the strain induced peak shifts.
Figure 53: Grazing angle XRD of Ni and Fe implanted PDMS thick film, with implantation carried out for 15 min (~17,000 shots) for each ion species. The increasing angle of incidence shows the strain induced peak shifts.

Figure 54: Grazing angle XRD of Ni and Eu implanted PDMS thick film, with implantation carried out for 15 min (~17,000 shots) for each ion species. The increasing angle of incidence shows the strain induced peak shifts.
Figure 55: Grazing angle XRD of Si implanted PDMS thick film, with implantation carried out for 15 min (~17,000 shots) for each ion species. The increasing angle of incidence shows the strain induced peak shifts.

Figure 56: Grazing angle XRD of Co implanted PDMS thick film, with implantation carried out for 15 min (~17,000 shots) for each ion species. The increasing angle of incidence shows the strain induced peak shifts.
In addition, the low incident angle scans were done at a number of angles of incidence to investigate the stress-strain mismatch between the multilayers and the internal stress of the stiff silicon rich layer, as well as the different strain properties of implantation with different metal ions. The grazing angle scans included high intensity, narrow peaks, consistent with the formation of thin textured silicate crystals on the surface. Such crystallisation is assumed to be the result of oxidation and subsequent decomposition. As expected, the surface features ensure that different incident angles display different silica peaks at different relative intensities.

The characteristic broad peak between 10 and 15 degrees, corresponding to the diffraction of small crystals of PDMS, also shows a very slight shift to the left, confirming the internal stress in the elastomer matrix as a consequence of the multilayers.

As shown by the peak shifts of Figs. 52, 53, 54, 55, and 56, and also summarised in Table 10, the mechanical differences between the adhered stiff silica skin and the elastomer matrix lead to a lateral force mismatch, resulting in surface undulations in the form of buckles as the silicon and oxygen rich layer undergoes compressive stress. To accommodate the induced mismatch strain between the skin and the elastomer substrate, the skin buckles in a wave-like manner, with wavelengths that are much larger than the stiff skin thickness and smaller than the overall dimensions of the elastomer base.

Table 10: Location of and shift in broad PDMS peak from grazing angle XRD as a result of surface strain.

<table>
<thead>
<tr>
<th>Composition</th>
<th>3 degrees</th>
<th>9 degrees</th>
<th>Strain Shift</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>11.67°</td>
<td>12.20°</td>
<td>0.53°</td>
</tr>
<tr>
<td>Ni, Fe</td>
<td>11.59°</td>
<td>12.43°</td>
<td>0.84°</td>
</tr>
<tr>
<td>Ni, Eu</td>
<td>11.67°</td>
<td>11.98°</td>
<td>0.31°</td>
</tr>
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</table>
Table 10 shows the differing effects on the internal stress between Ni implantation and a combined ion implantation. A lower strain shift leads to a decreased frequency of stress relieving V-shaped cracks, suggesting a method of further control over the formation of functionalised self-organising 3D surface features.

The high resolution SEM aspect of the surface presented in Fig. 57 shows nanosized holes, suggesting the possible evolution of a gaseous phase from the top layer of the film, consistent with the formation of methane. This is an indication that the energy delivered by implanting ions leads to the decomposition of the surface. Chenoweth et al\textsuperscript{281} demonstrated that at temperatures above 900 K and a fast heating rate, the degradation of the PDMS occurs through a radical mechanism involving Si-CH\textsubscript{3} homolytic bond cleavage, followed by hydrogen abstraction to form methane\textsuperscript{282, 283}, leaving a silicon rich layer. This is further evidence of structural modification in the top layer.

Figure 57: High resolution SEM image of surface porosity of the decomposed PDMS layer after ion implantation.
It should be understood that metal ion implantation of PDMS affects the chemistry of PDMS below the surface and beyond the implantation depth due to a continued energetic atomic interaction that result from the interaction between the energetic ion beam and the elastomer matrix. This occurs along with the influences on the bucking behaviour of the film in the modified silica like layer and the deposited metal rich layer. Cross-sectional TEM in Figure 58 shows the multilayer effects resulting from the metal ion implantation, which extend well beyond the 50-60 nm range of the implanted ions. Results of TEM energy dispersive spectroscopy (EDS) measured close to the surface, despite it being able to affect the local composition during the measurement, are shown in Table 11. The results are indicative of an increase in silicon and oxygen at the surface. Below that, there is a large metal rich layer with increased oxygen content, followed by a metal carbide layer, followed by a layer rich in silicates and oxygenated carbons. The approximate thickness of this modified zone is approximately 250 nm, and beyond the modified zone, there lies the unaffected poly-siloxane matrix. This multilayered variation in composition with depth is also supported by RBS. However, apart from the ionic properties introduced as a result of the metallic rich layer, it is widely understood that it is the surface and not the bulk properties that affect the biocompatibility.

Figure 58: Cross-sectional TEM conducted on a focused ion beam (FIB) lift-out from the iron implanted PDMS sample: a) pristine cross-section; b) EDS contamination spots indicate the regions where EDS was conducted from the surface into the bulk.
Table 11: Cross-sectional EDS results on iron implanted PDMS sample. Regions are indicated in Figure 31.

<table>
<thead>
<tr>
<th>Atomic Composition (%)</th>
<th>X1</th>
<th>X2</th>
<th>X3</th>
<th>X4</th>
<th>X5</th>
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</thead>
<tbody>
<tr>
<td>C</td>
<td>65.56</td>
<td>64.97</td>
<td>79.81</td>
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<td>72.24</td>
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<tr>
<td>O</td>
<td>8.82</td>
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<td>5.67</td>
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</tr>
<tr>
<td>Si</td>
<td>23.95</td>
<td>21.28</td>
<td>12.11</td>
<td>21.16</td>
<td>20.84</td>
</tr>
<tr>
<td>Fe</td>
<td>1.67</td>
<td>4.99</td>
<td>2.41</td>
<td>0.62</td>
<td>0.01</td>
</tr>
</tbody>
</table>

Cross-sectional TEM (Fig. 59) also confirms that, at the ion implantation potential used in this work, the range of implanted ions agrees with a SRIM calculation of a Gaussian depth distribution, with the peak at around 40 nm, and this was further confirmed by He RBS with the discovery of a deposited metal rich layer.

Figure 59: Cross-sectional TEM images of PDMS irradiated with Ni, Fe, and Au for 20 min, using an accelerating voltage of 50 kV and a beam current of ~ 1 mA. The black region is a metal coating grown on the surface as part of the focused ion beam (FIB) lift out process.

However, from the TEM cross-sectional images shown in Fig. 59, it appears that there are varying and distinct compositional layers in the polymer as a result of the
implantation, down to around 250 nm. This modification of the polymer matrix is deeper than the implantation depth of the metal ions. It has been speculated that this is due to further complex interactions between the polymer matrix and the energetic ions. It should again be noted that the depth and width of the metal rich layer, as well as the silica-like layer, has its own influence on buckling behaviour. Figure 60 shows the buckling behaviour of the films corresponding to the TEM cross-sectional images in Figure 59.

![Figure 60: Optical Images of PDMS irradiated with Au (left), Ni (middle), and Fe (right) with exposure to ions for 20 min, using an accelerating voltage of 50 kV and a beam current of ~1mA.](image)

Metal ion implantation of elastomers has been shown to be an efficient method of modifying their structure and electro-physical properties. A wide variety of material modifications of polymers have been studied by using ion irradiation techniques. Most studies have focussed on high-energy ions, probably because of the good controllability and the large penetration length in polymers. High-energy ion irradiation tends to significantly damage polymers due to the high deposited electronic energy of the ion, and chemical reactions in the polymers occur, such as ablation, sputtering, chain scission, cross-linking, and the formation of low molecular weight products.

Such ion bombardment of polymers can modify the structure, composition, and properties of surface material more readily than metals and ceramics. This is
because the bond strength of polymers is much lower than those of metals, ceramics, or semiconductors, which means that the energy transferred to electrons by incoming ions can stimulate chemical reactions. In short, ion beam irradiation leads to irreversible changes in polymers, and hence it is important to understand the damage mechanisms in polymers, with metal ion implantation yielding among the highest LET/nm values out of a variety of possible irradiation sources.

A consequence of the thermo-oxidative degradation of the surface of an elastomer film due to low energy metal ion implantation is the strain mismatch due to the coupling between the resulting stiff film and the unmodified elastomer bulk. This strain mismatch results in the creation of surface relief patterns due to buckling. Buckling provides an easy ‘bottom up’ way of using this self-organising effect to create and tune different topological structures on submicron to micrometer scales. Recent techniques to create 3D regular self-organised surface features on micron and submicron scales via buckling of PDMS surfaces include plasma treatment and oxidation, metal deposition, ion beam irradiation, and ionising radiation. This current work introduces and investigates a new mechanism of producing similar buckling behaviour to that reported previously for other methods, resulting from low energy metal ion implantation past a critical dose.

As well as for its usefulness in controlling the topographical regimes of buckling, metal ion implantation was chosen because it can also further functionalise the surface. Previous work has found that combining magnetic materials with wrinkling of PDMS can lead to magnetic correlations within the range of the buckling features. This has led to the creation of ferroscaffolds with unique topographical formations, which hold enormous potential as stimulus-responsive drug carriers and scaffolding materials for tissue engineering. Hu et al. found that the magnetic sensitivity of ferroscaffolds varied, exhibiting different degrees of magnetism, which could be further used to control growth factors for cell cultures. Similar behaviour within the range of the buckling features can be expected when
combining surface buckling with elemental functionalisation through metal ion implantation.

Magnetisation measurements were conducted on a 900 s Fe implanted sample of PDMS on a Si wafer with PPMS in a perpendicular field. When compared to magnetisation measurements conducted on a piece of unmodified PDMS film on a silicon wafer, an increased ferromagnetic response is evident (Fig. 61). However, only a very small ferromagnetic signal response is detected, due to this magnetisation measurement being a bulk technique. The volume of Fe in the insulating PDMS bulk is comparatively very small and easily drowned out by the polymer and Si wafer signal. In fact, this is nearing the limit of detection for this type of instrument.

Figure 61: Evidence of increased ferromagnetic activity as a result of implanted metal rich layer. Since PPMS is a bulk technique and the metal rich layer is small, the ferromagnetic signals are also relatively small. The small ferromagnetic signal coming from the pristine PDMS sample is an artefact.
An advantage of this method over other methods used to buckle the surface of elastomers is that it results in implanted element-rich micron-sized features. Previous work has shown that topography affects the elemental properties\textsuperscript{233}, as such metal ions can also be used to introduce desired functional behaviour into the 3D self-organised surface features. This work has used optically active and magnetic ions in functionalising these features. A variety of metal ions were used, including Ni, Co, Fe, and Eu, as well as combinations of them. The magnetic properties of Ni, Co, and Fe, and the optical properties of Eu are widely understood, and this method of producing buckling results in functionalised 3D surface structures with high elemental concentrations at the surface (Fig. 61).
5.1 Controlling the Buckling Regimes through the Use of Dose Effects

Surface buckling or wrinkling of the elastomer PDMS can be created in a number of different ways. These include plasma treatment and oxidation\textsuperscript{218, 226, 227, 228}, metal deposition\textsuperscript{186, 229, 230}, ion beam irradiation\textsuperscript{52, 224}, and ionising radiation\textsuperscript{232}. The control or tuning of the resulting buckling from these techniques has been achieved through controlling the properties used to induce buckling\textsuperscript{291, 228}, pre-patterning of the elastomer film\textsuperscript{218, 292, 186}, the use of masks\textsuperscript{293, 294, 226, 295}, or by selectively controlling the thickness of the film\textsuperscript{227}.

In the previous chapter, we have shown that modification of the surface of a thick PDMS film with implanted metal ions can induce complex buckling patterns, while also elementally functionalising the surface features. In this chapter, we have conducted a parameter study of this combined method of buckling and functionalisation, to understand the influence of various metal ion species, the varying geometric confinement of buckled areas on a larger unmodified elastomer film, and the boundary conditions imposed by the said geometric confinement on the induced buckling regimes, thereby creating a simple non-photolithographic means of patterning soft materials. Below are the results of the effects of varying dose on the buckling behaviour of the surface silicon- and oxygen-rich stiff film.

As shown in the previous chapter, buckling was induced onto an unstrained, unconfined PDMS film, such as was characterised above, to demonstrate the effects of low energy implantation of various metal ions at different doses. It was shown that the wavelength of this buckling is influenced by metal ion species. All of the implanted ions behaved similarly with dose, with the wavelength of the wrinkles rapidly increasing with increasing dose until a critical dose at which the increases in
wavelength started levelling off in a sigmoidal-like behaviour, as can be seen in Figure 62. The films implanted with the various ions start buckling at dramatically different wavelengths, which leads to a levelling off with time at different ranges, and with constant dose, the wavelength of the sine-like buckling pattern was found to be dependent on the metal ion species implanted. Since all implanted metal ions behave similarly in inducing wrinkling, albeit with different wavelengths, results for iron implanted PDMS are shown hereafter for consistency.

While it has already been shown that low energy ion implantation acts to decompose the surface of the elastomer to a silicon- and oxygen-rich stiff layer, thereby causing wrinkling behaviour due to strain mismatch, this does not explain the differences in the sigmoidal-like behaviour that is shown when different metal ions are implanted.

![Graph showing the dependence of wrinkle wavelength on the implanted metal ion.](image)

Figure 62: Dependence of wrinkle wavelength on the implanted metal ion. Ni, Ti, Eu, and Mg were also implanted at specific exposure times and found to follow the above sigmoidal trends.
It is speculated that the dependence of the PDMS wrinkle wavelength on the metal ion species is due to the metal-rich layer implanted into the elastomer matrix. Once implanted, the metal ions act to form either a homogeneous metal-rich oxide composite layer or a layer of metallic clusters suspended within the elastomer matrix beneath the decomposed stiff layer. The thickness and depth of this metal-rich layer is dependent on the dose and penetration depth of the metal ions implanted. This conclusion is supported by previous work done on metal ion implantation in polyethylene terephthalate\textsuperscript{32, 33}.

Figure 63 and 64 provides a SIMNRA model and experimental data showing the depth profiling of this metal layer within the PDMS matrix of Co and Fe implanted films with exposure times of 1, 2, and 3 minutes. It is confirmation that the different metal ions produce different layer profiles in agreement with the theory.

![RBS spectra of metal ion implanted PDMS films showing the presence of a metal rich volume within the polymer matrix.](image-url)
Figure 64: RBS profiles of the metal layers in PDMS thick film for 1, 2, and 3 min exposure times. Note: the 3 minute exposure for Co is missing, since RBS showed a step rather than a peak.

Earlier glancing angle XRD results (Figs. 52-56), which showed that different ion species introduced different amounts of strain into the surface layer, along with initial cross-sectional TEM of Ni, Fe, and Au implanted PDMS, demonstrated that various depths and thicknesses of metallic rich layers could affect the wavelength. Unlike Fe, Co, and Ta, Au only has 3 data points, so it is possible that the trend may be dissimilar, although the authors think this unlikely.

This allows for another parameter for the control and manipulation of buckling and of both wavelength and amplitude, in both dose and the selection of the metal ion, enabling this method to become a realistic bottom-up measure for creating a variety of 3D surface relief morphologies for scientific and technological applications.
5.2 Controlling the buckling regime through the use of masks

A parameter study was conducted to study the dependence of the complex buckling regimes on implanted metal ion species, dose, and varying geometric confinement of buckled areas onto a larger unmodified elastomer film, and the boundary conditions of said geometric confinement through circular islands of different sizes. So, with the use of a mask, islands of buckling were induced onto a larger PDMS thick film confined to a Si wafer to investigate the role that geometric confinement plays in selective control over the buckling regime.

The evolution of buckling with increasing dose is a little different when it is geometrically confined with the use of a mask, as opposed to implanting the entirety of a large surface. When the entire surface is implanted, as the implantation dose increases, the frequency of the V-shaped cracks, the wavelengths of the buckles, and the density of buckling also increase, until reaching a saturation point after which no further increase in buckling density is seen. The V-shaped cracks, defects, voids, dust particles, and even edges on the surface serve as initiation sites for the buckling, which upon higher doses, quickly branches out to completely cover the surface of the exposed films in a semi-chaotic pattern of herringbone ripples. When geometrically confined (Fig. 65), there is often a lack of V-shaped cracks, and buckling occurs in the centre of the implanted region, again initiated at defects, voids, and dust particles, branching out with increased dose in a self-organised manner until distinct morphological regions, characterised by radial and hooping buckling, have been established.
Figure 65: Optical microscope images of the evolution of buckling in a circular island with increased dose of iron implantation. Exposure times are 5 s (a) and 30 s (b).

Geometric confinement also plays a role in controlling the wavelength of the sine-like buckles within the islands. There was a linear decrease in the wavelengths of the buckling with increasing island size. There was an approximately constant 3 μm increase for all metal ions tested, in wavelengths recorded between the buckling at the centre of the island and that at the edge of the island. This suggests that there is a radial strain that increases linearly from the centre of the island to the edge as a result of the use of a mask. With small islands, we can treat the implantation process as homogeneous across the island, ruling out any gradient effect resulting from the metal ion implantation.

This persistence of the aligned radial buckling at the edge of the island is due to the azimuthal strain from the implanted ions, which is induced by circumferential pressurization at the boundary due to the unmodified PDMS elastomer and the modulus mismatch. This leads to increases in the length of aligned radial buckling to the edge with dose, as shown in Fig. 66, but decreases with increased island size.
Figure 66: Au implanted PDMS thin film with 20 min of exposure in a 1 mm radius spot. The buckling wavelength at the edge of the spot is 3 μm larger than the wavelength at the centre of the spot.

It was discovered that even the aligned radial buckling at the boundary of the ion implanted spot can be controlled by altering the pressurization conditions by making the boundary irregular. Figure 67 shows a spot with an irregular boundary and what effect this has on buckling initiation. Rather than aligned buckling right to the edge, it is initiated well into the spot, except in regions of the boundary that can be described as at right angles to the buckling.
Figure 67: Buckling pattern seen for a 5 s Fe ion implanted spot on a PDMS film. The effects of an inhomogeneous edge can be seen on the buckling initiation.

In the interior of the implanted islands, away from the geometrically confined, radially aligned buckling, random self-organised coherent and semi-coherent buckling morphologies were seen to form. As the strain increases, the morphology makes a transition from radial and hooping zigzag patterns, to “telephone cord” buckling. This leads to a pattern of polygons in spots where random buckling intersects (Fig. 68).
Figure 68: Semi-coherent buckling pattern as a result of 20 min Au implantation with a mask on a PDMS film on a supporting Si wafer.

Figure 69: Optical microscope images of the different buckling morphologies as strain increases: a) radial and hooping zigzag patterns from 5 s Fe implantation; b) telephone cord buckling from 20 min Fe implantation; c) random buckling fronts intersect, leading to a pattern of polygons bounded by telephone cord buckling in 20 min Fe implantation.

Unmentioned so far, has been the possibility of using a shadowing effect from the ion implantation to create useful morphologies. Through clever mask design, the shadowing effect resulting from the distance of the mask from the film allows a small area immediately outside the island to receive a fraction of the dose of the exposed island. This allows the creation of specific strain minimisation effects outside the buckled island, dependent on the dose and radius of curvature of the
island boundary, which results in a buckling morphology that is significantly different from that inside the island.

Figure 70 shows two different radius of curvature boundary conditions, where islands of different sizes implanted with identical doses of Fe implantation have led to entirely different morphologies. The two radii of curvature below (Fig. 70) also highlight the evolution of the edge effect outside the edge of the buckled island, with the first panel (Fig. 70(a)) showing a large radius of curvature, with an island size of 5 mm, giving the impression of an almost straight line at the given scale, and a smaller radius of curvature (Fig. 70(b)), with an island size of 1 mm, which at the same scale appears discontinuous.

![Figure 70: Optical microscope images of two different radius of curvature boundary conditions, for identical dose of Fe implantation, resulting in different strain buckling: a) large radius of curvature (island radius 5 mm) leading to three distinct regions of strain at the outside of the implanted island; b) small radius of curvature (island radius 1 mm) with lower strain, showing the beginning of the buckling edge effects; c) and d) AFM height profile results from across the edge of the larger and smaller metal ion implanted islands, respectively.](image)

Figure 70: Optical microscope images of two different radius of curvature boundary conditions, for identical dose of Fe implantation, resulting in different strain buckling: a) large radius of curvature (island radius 5 mm) leading to three distinct regions of strain at the outside of the implanted island; b) small radius of curvature (island radius 1 mm) with lower strain, showing the beginning of the buckling edge effects; c) and d) AFM height profile results from across the edge of the larger and smaller metal ion implanted islands, respectively.
Figure 71: The edge of a large 20 min Fe ion implanted spot. The buckles within the spot can be seen to be bordered by nano-pillars, and then outside the spot, there are micro-buckling patterns an order of magnitude smaller than that seen within the spot away from the edge.

Figure 72: The edge of a large 20 min Mg ion implanted spot. The buckles within the spot can be seen to be bordered by nano-pillars, and then outside the spot there are micro-buckling patterns an order of magnitude smaller than that seen within the spot.
Figure 70 also serves to highlight the evolution of buckling, outside of the masked spot, with increasing strain. There are three regions of strain clearly delineated, and this behaviour is similar for all island sizes and metal ion species: there is one region including the first 20 μm closest to the edge, followed by a different alignment for another 80 μm out, followed by random buckling. Using these relationships, and by regulating the dose and the curvature of the boundary through island size, different buckling regimes of determinable length, both within and outside the island, can be manufactured as part of a larger-scale buckled system, where a variety of buckling regimes are needed within a single system. Usefully, the shadowing effect can be further controlled when two shadowing effects are placed in proximity. An approximately 50 μm wide field of 2 μm buckles has been established with wavelengths that are an order of magnitude smaller than the buckling seen in the exposed island region.

Since all of these parameters are fairly easy to control, a combination of geometric confinement through the clever selection of masks, dose, and metal ion species would allow the engineering of several different buckling regimes, with different elemental functionalisation of 3D features within a global buckling system. This remains a large advantage of this method of buckling for easy ‘bottom up’ creation and tuning of different topological structures on submicron to micrometer scales for use in a variety of scientific and technological applications.
Part 6: Functional uses and applications for low-energy metal implanted PDMS surfaces

6.1 Functional evaluation of buckled surfaces for biological applications

Polydimethylsiloxane (PDMS), a durable silicon-based organic polymer, is widely used as an optically clear, flexible, inert, non-toxic, and non-flammable biocompatible material. The siloxane linkages allow PDMS molecules to flex, and adjusting the curing ratio can vary this flexibility. As such, PDMS is routinely used as a biomedical implant material, as a substrate for microfluidic device and cell array fabrication and for fundamental cellular studies, however, the low surface energy and hydrophobic nature of PDMS inhibit its bioactivity. This non-optimal biocompatibility has been addressed through biochemical coatings and physico-chemical treatments of the elastomer, including surface grafting, plasma discharge using various gases and excitation frequencies, corona discharge, laser ablation, microwave irradiation, and UV modification. These types of treatment have been widely used to improve the cellular adhesion on silicone surfaces by affecting the wettability of the elastomer surface. We have proposed and investigated the usefulness of a simple, one-step, low energy metal ion implantation method as a way to improve the bio-activity of selected regions of a PDMS substrate.

First, we consider results of the XPS analysis. For the pristine, untreated PDMS material, the XPS results show the positions of C1s and O1s lines (at 282.8 eV with a FWHM of 1.44 eV, and at 530.7 eV with a FWHM of 1.55 eV, respectively), which is consistent with C-Si-O-Si and O-Si-O-R bonds, respectively. This is indicative of a polysiloxane structure, as expected. Upon metal ion implantation, the C1s line shifts to a higher energy and broadens, indicating an increase in oxidised carbon species; at the same time, the increase and broadening of the Si2p peak to 100-101 eV is
consistent with an increase in silica and carbide containing species. The oxygen peak at about 531.1 eV is characteristic of hydroxides and carbonates.

Table 12: XPS atomic composition analysis of native PDMS and metal ion implanted PDMS.

<table>
<thead>
<tr>
<th></th>
<th>Binding Energy (eV)</th>
<th>Peak Width (eV)</th>
<th>Atomic Composition (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Native PDMS</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O 1s</td>
<td>530.7</td>
<td>1.6</td>
<td>26.5%</td>
</tr>
<tr>
<td>C 1s</td>
<td>282.8</td>
<td>1.4</td>
<td>41.6%</td>
</tr>
<tr>
<td>Si 2p</td>
<td>100.5</td>
<td>2.1</td>
<td>31.9%</td>
</tr>
<tr>
<td><strong>Mg Modified PDMS</strong></td>
<td>531.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O 1s</td>
<td>531.1</td>
<td>1.7</td>
<td>37.8%</td>
</tr>
<tr>
<td>C 1s</td>
<td>283.2</td>
<td>1.7</td>
<td>30.9%</td>
</tr>
<tr>
<td>Si 2p</td>
<td>101.3</td>
<td>2.2</td>
<td>31.3%</td>
</tr>
<tr>
<td><strong>Ta Modified PDMS</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O 1s</td>
<td>531.1</td>
<td>1.8</td>
<td>35.6%</td>
</tr>
<tr>
<td>C 1s</td>
<td>283.4</td>
<td>1.8</td>
<td>38.0%</td>
</tr>
<tr>
<td>Si 2p</td>
<td>101.2</td>
<td>2.1</td>
<td>26.4%</td>
</tr>
<tr>
<td><strong>Fe Modified PDMS</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O 1s</td>
<td>531.1</td>
<td>1.7</td>
<td>35.2%</td>
</tr>
<tr>
<td>C 1s</td>
<td>283.2</td>
<td>1.8</td>
<td>24.0%</td>
</tr>
<tr>
<td>Si 2p</td>
<td>101.3</td>
<td>2.1</td>
<td>30.0%</td>
</tr>
<tr>
<td><strong>Au Modified PDMS</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O 1s</td>
<td>531.2</td>
<td>1.7</td>
<td>37.5%</td>
</tr>
<tr>
<td>C 1s</td>
<td>283.2</td>
<td>1.9</td>
<td>35.1%</td>
</tr>
<tr>
<td>Si 2p</td>
<td>101.4</td>
<td>2.2</td>
<td>23.8%</td>
</tr>
</tbody>
</table>

Relative atomic concentrations calculated from peak areas are shown below in Table 12, indicating a general increase in oxygen content along with a relative carbon content decrease with sample treatment. No metal ions were detectable at the surface; we suggest that this is because metal ions penetrate deep below the
surface of the PDMS material, while XPS probes only about 5 nm of the top layer. This is consistent with the Rutherford Backscattering (RBS) data showing an average implantation depth of over 50 nm, consistent with SRIM calculations.

Further insight into the surface chemistry upon ion-implantation can be seen from the consistent increase in O/C and Si/C ratios calculated and shown below in Figure 73, reinforcing the evidence that there is bonding of Si, O, and C in the surface. An increase in silicon, carbon, and oxygen species at the surface further supports the view that the energetic implanted metal ions act to break the silicon-carbon bonds through scission, allowing for the formation of a stiff film consisting of carbides, hydroxides, and oxygen rich silicon species on the surface. These results are similar to other studies of surface modification as a result of irradiation, such as those obtained both for oxidising plasma\textsuperscript{299, 300, 301} and surface coating using magnetron sputtering\textsuperscript{302}.

![Atomic elemental composition Ratios](image)

Figure 73: O/C and Si/C ratios for the surface of pristine and metal ion implanted PDMS.
As expected, Fig. 74 shows the contact angle decreasing with implantation dose up to the maximum dose used in this study. It has been demonstrated earlier that past a critical dose, the surface of the elastomer film starts to pyrolytically decompose to a silica-like layer, below which are multiple layers of varying composition from increased PDMS cross-linking to metal rich layers. As part of this surface modification process, and as confirmed by XPS, an increase in hydrophilic functional groups is seen with increased dose, and this translates to a decrease in the contact angle with water droplets with dose, as seen in Fig. 74.

![Contact Angle Graph](https://via.placeholder.com/150)

Figure 74: Contact angle decreases with increasing exposure to energetic metal ions.

As well, a variation in the decrease in contact angle is seen with different metal ion species. The contact angles decreased from 110° for pristine PDMS to 18° for Mg implanted PDMS, as shown in Figure 75, while in the Fe implanted sample, it only decreased to 80°. This increased hydrophilicity of the modified PDMS surfaces is consistent with the increased hydrophilic functional groups in the polymer chains and/or the formation of oxidation products of low molecular weight on the polymer surface, as demonstrated earlier by XPS of the surfaces. Figure 75 compares the
contact angle of native and modified PDMS to those of some other readily used surfaces in cell culture work. Glass and PMMA were obtained from the literature\textsuperscript{303}.

![Bar chart showing contact angle of native and modified PDMS in comparison with glass and PMMA.](chart.png)

Figure 75: Contact angle of native and modified PDMS in comparison with some other commonly used surfaces in cell culture work, glass and PMMA.

As expected, this change in surface chemical composition and corresponding modification of side groups, leading to an increase in polar groups, has an effect on the surface energy. The increase in the polar component of the surface energy, calculated from the geometric mean, results in up to a tripling in total surface energy between native and modified PDMS. Again, it is shown that the increase in hydrophobic functional groups with dose leads to and increases the polar component of the surface energy with varying effectiveness. Au implanted PDMS film shows a greater effectiveness than Fe implantation at increasing this polar component, which is reflected in the contact angle differences.
Figure 76: Surface energy increase with increased dose. This is consistent with an increase in surface polar groups as a result of pyrolytic decomposition.

Figure 77 shows the surface energy of native and modified PDMS in comparison with some other readily used surfaces in cell culture work, glass and PMMA. The PDMS films were implanted with metal ions at the same exposure times. This further highlights the difference in effectiveness in terms of generating and stabilising surface hydrophobic functional groups between the implanted metal ion species. Again, it is speculated that this is a result of both the atomic interactions of the energetic ion species on the surface and the differences in the thickness and depth of the metal rich layer that results from the ion implantation process.
Figure 77: Surface energy of native and modified PDMS in comparison with some other readily used surfaces in cell culture work, glass and PMMA

Figure 78 shows optical microscope and fluorescence images of representative areas of the modified and unmodified PDMS surfaces, demonstrating the dramatically improved surface for cell growth and proliferation as a result of the induced changes in surface energy, surface chemistries, and topology resulting from low energy metal ion implantation. These and other representative images taken from samples within different wells were used to create a data mean count of viable cells, which was taken and normalised against the mean cell count for the pristine PDMS surface. A significant 632% increase in cell count was seen for the Fe implanted sample compared to the untreated surface (Fig. 78(a)), with Mg and Ta recording a 447% and 463% increase, respectively.
The spatial organization of cells plays a critical role in fundamental biological studies, as well as in the development of tissue engineering scaffolds, biosensors, and microfluidic assays. The production of simple, cost-effective substrates for cell patterning would thus have benefits for numerous areas of bio-analytical research, including tissue engineering and biosensor development. Commonly, to facilitate selective cell patterning, a combination of surface functionalisation with adhesion promoting and inhibiting molecules and pre-patterned substrates are used. Biochemical coatings, such as coating with extracellular matrix proteins allows for the enhancement of interactions between the materials and the cells through the promotion/regulation of cellular functions such as adhesion, migration, proliferation, and differentiation.
Besides being time consuming and costly, this method of selective patterning requires multiple processing steps, complex chemistries, and clean room facilities. Although features with sub-micrometer resolution are possible, the monolayer modifications that result are often too fragile to withstand physiological or microfluidic shear stresses, thereby limiting their long-term use in device applications\textsuperscript{79}. As well as coatings to guide cell growth, it is relatively well known that the surface topography of a polymer has an impact on cell adhesion and cell growth because the microscale texture of a surface significantly affects the cell adhesion behaviour on the surface. Recently a number of studies have focused on micrometer-scale topographies such as grooves, ridges, pits, and islands\textsuperscript{107, 108}. The width and the depth of the surface topographical structures can also influence cell responses, since cells can orient themselves along the grooves and the ridges in a behaviour called ‘contact guidance’\textsuperscript{95, 96}. In some cases topographical effects have been found to be more important for cell adhesion than surface hydrophilicity / hydrophobicity.

It has been shown in previous work\textsuperscript{298}, that low energy metal ion implantation can be used to modify the surface of PDMS into different functionalised 3D morphologies, within a global system of buckling by inducing discreet regions of strain, without the effort of pre-patterning the substrate. This is done through the control of the metal ion species, the dose, and the geometric confinement of the buckled area and the boundary conditions by the use of masks.

Based on this approach, we show the benefits of the modified surface properties of PDMS in terms of increased biocompatibility for selective cell growth without the need to use biochemical proteins and molecules. The ease with which dominant and complex patterns can be generated and controlled on the surface of an elastomer film makes self-organising buckling an easy ‘bottom up’ way of creating and tuning different topographical structures on submicron to micrometer scales for such applications. This potentially provides a simple and inexpensive technique for rapid and reproducible selective cell patterning of substrates for tissue
engineering, without the need for any pre-treatment of the elastomer such as stretching or coating. Selective low energy metal ion implantation with the use of an aluminium mask acts to selectively create regions of increased bioactivity in a self-organised and complex pattern though the control of implantation dose, mask boundary conditions, and constrained regions of buckling.\(^{304}\)

As well, the modifications of such elastomer surfaces, chemically and topologically, have a variety of scientific and technological applications that range from mechano-transduction, tissue engineering, and regenerative medicine, which rely on altering surface topology and controlling the mechanical environment, to microfluidics and lab-on-chip devices, to building memory storage devices, stretchable electronics, optical diffraction gratings, optical micro-lenses, and biosensors.

In the field of mechano-transduction, tissue engineering, and regenerative medicine, surface modification is particularly important, since cells are sensitive to all length scales from macro to molecular, and the manipulation of the cell – material interface is critical to controlling and manipulating cellular growth.\(^{309,310,311}\)

When engineering the surface of a material to optimise the cell material interface, it is useful to keep in mind that cells respond to three broad categories of surface physiochemical cues which effect growth, differentiation, and other cellular processors: chemical, topographical, and mechanical. It also well recognised that it is the surface, rather than the bulk properties of the material that provide these cues, no matter how useful the bulk properties of the material may be in implanted devices, such as low density and thus reduced weight, elasticity, and chemical inertness.

Systematic studies have been conducted on the impact of surface chemistry and topology of the surface of different materials on its biocompatibility. Since
cells are sensitive to all length scales from macro- to molecular, surface modification is integral to the manipulation of the cell – material interface which is critical to controlling and manipulating cellular growth\textsuperscript{309,310,311}. On modifying the surfaces of polymers by the use of ion implantation, by changing ion species, energy, and dose, the mechanical properties of the surface properties of PDMS can be engineered with equal ease to its surface chemistry and topology, more so than any other material.


6.2 Possible example for use of buckled elastomer thick film - Multi-electrode Array Recording System

The implementation of technology for achieving stable interfacing of external electronics to bio-electrically active tissues and single cells requires the basic functionality and the survivability of cellular cultures to be optimised and the electrical Signal to Noise Ratio (SNR) maximised between the electronics and the electrically active biological system.

Applications of technology that can effectively and repeatedly achieve stable interfacing between external electronics to bio-electrically active tissues and single cells require research in the areas of biomaterials, pharmacology, and neuronal and artificial intelligence.

Of particular interest when interfacing bio-electrically active tissues and electronics is the temporal and spatial behaviour of the electrical activity within the cellular network in a multi-channelled approach. This way, both individual cells and cell networks can be scrutinized in order to understand how changes in single unit activity shapes network operation and development.

In the field of neuronal engineering there are a number of methods used to culture, record, and stimulate biological networks on an electronic system. These include the multi-electrode array (MEA) approach, the natural field-effect transistor (FET) approach, and an approach involving patch clamping.

Multi-electrode array technology is almost three decades old and yet holds promise in the study of network level information processing in the nervous system, and in plasticity and artificial intelligence. MEA technology makes use of substrate-integrated electrodes to make multi-channel extracellular recording and stimulation of cultured neurons possible. This technique can be used to seek bidirectional interfacing with all the neurons within a cultured neuronal network.
microcircuit individually and over long periods of time. Although extracellular recordings suffer from lower signal to noise ratios (SNR), the minimum invasiveness allows for long term recording, and the multi-microelectrode capabilities permit studies on large networks.

As opposed to the MEA method, the natural FET method involves growing the neuron into the silicon chip as the gate of a metallised FET. Neuro-electronic interfacing is, out of necessity, achieved via a two-step process, with the first step determining the flow of current within the core-coat conductor, while the second is the detection of the transductive extracellular potential (TEP) that is produced in the core coat conductor via voltage sensitive devices. This is made possible through the creation of a circuit on the silicon substrate surface.

Alternatively, patch-clamp recording and stimulation of synaptically connected neurons is a well-understood method of charge transfer that requires accurately machined holes and complex fluidics. While this is a very good method for investigating small and uncomplicated networks, it is not very feasible for more complex neuronal networks. Its invasiveness also inhibits its feasibility for long-term recording.

For the purposes of this study, MEA technology is the most suitable for establishing multi-channelled bidirectional communication capability. Bidirectional communication between a cultured bio-active neuronal network and external electronics such as a MEA is especially interesting, since neurons can establish and change their connections and vary their signal properties according to a variety of rules. Because many of these changes are driven by spatial and temporal patterns of neuronal signals, neuronal networks can adapt to circumstances, self-assemble, auto-calibrate, and store information by changing their properties according to experience. It is possible to predict the optimal geometric patterns of connectivity, including the optimal ratios of axonal and dendritic arbour volumes.
Nature has an important advantage over electronic circuits because components are connected by wires (axons and dendrites) in 3D space, whereas even the most advanced Very Large Scale Integration (VLSI) microprocessor chips use a small number of layers with planar wiring. For example, 3-D cultures that are assembled from dissociated cells form in-vivo-like structures, exhibit in-vivo-like responses to stimuli, and survive longer than monolayer correlates. In addition, research on cortical slice preparations in vitro is presently limited to thin (~500 µm) cultures that do not include all the layers or lateral dimensions, although the structural organization of the cortex may be the key to its vast information storage and processing capabilities.

In established planar multi-electrode arrays (pMEA) systems, such as the one used below, Indium Tin Oxide (ITO) conductors are covered by 3 µm of polysiloxane resin before the 64 electrodes at the centre of the plate are de-insulated and gold plated for reduced impedance. This elastomer coating is used both as an insulating material to minimise neuronal crosstalk as well as to act as a patterning material to guide growth of neuronal networks only to areas where there are electrodes present that are available for bidirectional communication.
As we have demonstrated through the low energy metal ion implantation of PDMS thick films, it is possible to induce and control buckling, and also selectively create regions of varying biocompatibility. This has the potential to increase the effectiveness of pre-existing pMEA systems by creating and manipulating 3D relief structures with varying biocompatibility for increased control over the special organisation of cells in a network. This simple and inexpensive technique for rapid and reproducible selective cell patterning on substrates into 3D patterns is a simple and inexpensive technique, without the need for any pre-treatment of the elastomer such as stretching or coating.

Since the main focus of this work has been in the low energy metal ion implantation of PDMS surfaces for a new bottom up method of creating 3D microstructures, limited work has been done with this system. Below, we have successfully set up a working pMEA system in preparation for further work in this area.
5.2.1 Experimental

The general Recording Array Technology (RAT) system, which was designed by microelectrodesystems, to record evoked field potentials and spikes from brain or cardiac tissues using a 64 multi-electrode array (http://multimicroelectrodesystems.com/), was purchased and installed. The components consist of a micro-electrode chamber, as shown below (Fig. 80), preamplifiers (×50), a preamplifier break-up box (PBOB) and a hardware digital filter box (including a Post-amp ×50, and a two pole 5 kHz low pass filter). The data was then acquired with the use of a Data Acquisition Board (PCI-6071) and software that was also designed by microelectrodesystems for data acquisition.

In addition to this set-up, excess electromagnetic noise present in the laboratory, both ambient and through the power supply, necessitated the installation of a bronze faraday cage and a power shield defender (650 VA) uninterrupted Power supply (UPS) to reduce the recorded background noise to 30-40 μV P-P, allowing the recording and analysis of spikes greater than and equal to 40 μV P-P. The entire set-up was placed on an inverted microscope stage for active viewing for the duration of the electrophysiological recording. A hole was cut into the bottom of the cast aluminium box to ensure an unobstructed view of the cell culture during recording.

The components that most affect the cell culture are the glass MEA containing the neuroblastoma, the stainless steel chamber block that is used to contain the cell media during electrophysiological recording, and the heated cap in place to prevent condensation and allow the maintenance of 5% CO₂ in the air environment. 5% CO₂ in air (premixed gas) was allowed to flow into the cell chamber to ensure an appropriate atmosphere for cell culture during recording. This was achieved through a slight positive pressure within the cell recording chamber.
Figure 80: (a) Base plate with heating resistors and an aluminium chamber block fastened with thumbscrews. MEA is connected to board with zebra stripes. (b) Electronics and base plate placed into a cast aluminium box with small hole cut out above and below chamber for visibility. (c) SH-SY-5Y cells adhered to a MEA with cell medium in a petri dish. Gasket is removed and the MEA is placed in the chamber block. (d) Cast aluminium box is placed onto a microscope stage with entire setup placed inside a Faraday Cage for the recording of bio-electrical signals from the cell culture.

SH-SY5Y cells were cultured in a culture flask before trypsinizing and reseeding at a low density on a prepared glass MEA for later recording. The MEAs that the cell cultures were attached to, providing the integral electrophysiological substrate, were obtained from the Centre of Network Neuronal Science (MMEP; CNNS, Denton, TX).

The preparation and fabrication of the MEA are described in detail in numerous publications, such as Gross, 1979; Gross et al., 1985; Gross and Kowalski, 1991; Gross, 1994. However, briefly, the MEA is a 500×500×1 mm³ soda-lime glass plate covered with 1,000 Å of quartz. Indium tin oxide (ITO) conductors are covered by 3 μm of polysiloxane resin before the 64 electrodes at the centre of the
plate, occupying a recording area of ~1 mm$^2$, are de-insulated and gold plated for reduced impedance.

Once the MEA is in place within the RAT system, data acquisition is controlled by the RAT software (http://multimicroelectrodesystems.com/). This software allows for the recording of a variety of variables on all 64 channels, including timestamps and spike amplitude, for non-live analysis. Recording resolution and gain are readily controllable.

Figure 81: 64 electrode MEA used in RAT system for the recording of evoked field potentials and spikes: (a) entire 5x5 cm glass plate displaying ITO tracks; (b) ~1mm recording area showing the 64 electrodes.
5.2.1.1 MEA Preparation

The day before seeding the SH-SYSY cells onto the glass MEA plate, the plate was thoroughly cleaned with 95% ethanol and cotton, removing all traces of previous experiments, both cell debris and residual silicon grease. The rubber gaskets were cleaned by scraping with a razor and soaking in 95% ethanol.

Once clean, the gasket is lined with a layer of silicon grease and pressed firmly onto the MEA to form a bio-neutral water tight seal. Both the MEA and the gasket are then sterilized under wet heat by placing them face up in an autoclave at 121°C for 30-40 minutes (standard autoclave cycle). During this cycle, the silicon grease seal may become puckered and the watertight seal broken, but by re-pressing the gasket onto the glass slide, the seal can be readily re-obtained.

Surface preparation then involves the flaming of the surface of the MEA with the blue flame of a butane torch. This changes the hydrophobic polysiloxane insulation material into a hydrophilic surface ready for the addition of adhesion molecules.
during cell growth. Flame treatment is a non-specific surface functionalisation method that bombards the polymer surface with ionized air, generating a broad spectrum of surface oxidation products in the top several monolayers\(^3\). In this method, the reactive oxygen is generated by burning an oxygen rich gas mixture. Flame treatment has been shown to impart hydroxyl, aldehyde, and carboxylic acid functionalities to poly(ethylene) and is utilized to enhance printability, wettability, and adhesion.

This allows the flamed surface to accept adhesion molecules and cell suspensions. The blue tip of the flame is briefly in contact with the recording area, creating a sufficiently large area for the cells to be seeded in a low density monolayer. This is important, since too high a cell density can create a situation where cell-cell adhesion is greater than cell substrate adhesion – leading to cell clumping. Cell clumping creates a problem because of the ease with which the cells detach themselves from the MEA while it is being loaded into the RAT system.

### 5.2.2 Results and discussion

With live cellular cultures there is always quite a high risk of microbial contamination, with the lines of contamination quite broad. While autoclaving of equipment and electrophysiological substrates eliminates most sources of microbial contamination, contamination from bacteria, fungi, yeasts, and mycoplasma is still possible.

Bacteria were the most common source of contamination for the cellular cultures in this work, and while a small concentration of Penicillin-Streptomycin is used to mitigate the risk of microbial contamination, too high a concentration affects the rate of cellular growth and has been known to affect the electrophysiological behaviour of neuronal cultures. It has been the practice, as mentioned above, to culture SY-5Y cells in a larger beaker before trypsinizing them and seeding them on the glass pMEA to allow them to settle and adhere to the surface. However, as seen
in Fig. 83, when the cell density is too high, cell clumping is seen, which affects the electrical signals recorded by the MEA by introducing a large amount of electrical crosstalk.

Figure 83: Cell density too high, resulting in significant cell clumping.

For this reason, a lower number of cells are seeded onto the pMEA and allowed to adhere and spread to the flamed surface overnight. This gives a lower number of cells over each electrode, as in Fig. 84, which allows for a cleaner recorded signal or spike.
Excess electromagnetic noise that was present in the laboratory, both ambient and through the power supply, was an issue initially. This often produced high levels of noise in the system, completely disguising all spikes resulting from bio-electrically active cellular networks, as well as producing false positive spikes. The installation of a bronze Faraday cage and a power shield defender (650 VA) UPS effectively solved this problem and also ensured that the recorded background noise was reduced to 30-40 μV P-P (Fig. 85), allowing the recording and analysis of spikes greater than and equal to 40 μV P-P.
Figure 85: 4 representative electrodes showing the continuous background noise component.

Although all 64 channels were not working at all times due to the failing of individual electrodes, the system showed spike train activity from the cellular cultures, demonstrating that the system was ready for future work on implementing the buckling of the elastomer layer around the pMEA array for organised neuronal networks (Fig 86).
Figure 86: Selected spike activity captured from the RATS software.
Part 6: Conclusion

Polydimethylsiloxane was selected for suitability as a non-biodegradable scaffold or support for use in the creation of artificial and semi-artificial soft tissue organs. The appropriateness of polydimethylsiloxane for this application has been further enhanced through the treatment and subsequent modification of the surface with low energy metal ion implantation. This treatment and modification adds further functionality to this already widely used biomaterial through the production and control of complex micrometer-scale topographical patterns on the surface and also the selective enhancement of the bioactivity of the surface through the introduction of complex polar functional groups to the surface.

Changes to the chemical composition and strain of the surface layers of the modified PDMS thick films have been induced through low energy metal ion implantation. We have successfully shown that ion implantation can be used to modify the surface of PDMS by inducing buckling through the decomposition of the surface of a PDMS thick film. Metal ion implantation causes significant internal stress within this stiff upper layer, which causes V-shaped cracks to form randomly, with an ordering of the buckling around these points. The buckling is disordered away from any V-shaped cracks, forming partial domains.

It has been demonstrated that the internal stress can also be controlled through not just the ion implantation dose, but also by using a variety of metal ions, thus allowing for higher concentrations of functional metal ions. Low energy metal ion implantation can be used to modify the surface of PDMS into different functionalised buckling morphologies, within a global system of buckling, by inducing and directing discreet regions of strain without the effort of pre-patterning the substrate. This is done through the control of the metal ion species, the dose, and the geometric confinement of the buckled area and the boundary conditions by the use of masks. This allows for a rapid and versatile ‘bottom up’ way in which to
create discrete topological morphologies for use in the selective modification and control of the surface topology of elastomers for future applications such as degradable biomedical devices, including surgical dressings, vascular grafts, tissue engineering scaffolds, sutures, and structures for guided tissue regeneration.

In fact, this single-step, rapid prototyping technique has proved able to produce both complex micrometer scale topographical patterns and also increase the bioactivity of the surface significantly. All of the metal ion modified surfaces enjoyed an increase in attached viable cells of over 450%, with the Fe implanted surface showing a 600% increase. This follows a large increase in the O/C and Si/C ratios at the surface, as well as a dramatic increase in hydrophilicity, with the polar component of surface energy increasing to 50 mJ/m$^2$ as a result of low energy metal ion implantation. The ease of creating regions of varying surface energy and chemistries on a single substrate makes this technique useful for the creation of selective and functionalised substrates and scaffolds for in-depth bio-analytic studies, implants, and device components.

Thus a single step, rapid prototyping technique has been demonstrated that lends itself to the production and control of complex micrometer-scale topographical patterns on the surface, as well as to the selective increase and control over surface biocompatibility without the need to use biochemical proteins and molecules, or other complex surface modification methods. This is achieved through the control over the hydrophobic recovery of the surface over time through the implantation of metal layers with a variety of depths and thicknesses. The ease of creating selected regions of varying surface energy and chemistries on a single substrate for controlled micrometer-scale topological patterns makes this technique useful for the creation of selective and functionalised substrates and scaffolds for tissue engineering applications such as artificial and semi-artificial soft tissue organs, in-depth bio-analytic studies, implants, and device components.
Appendix 1: Published works

Structural and morphological modification of PDMS thick film surfaces by ion implantation with the formation of strain induced buckling domains

B. R Winton, M. Ionescu, S. X. Dou, D. Wexler, G. A. Alvarez

Keywords: implantation, atomic force microscopy (AFM), scanning electron microscopy (SEM), x-ray diffraction (XRD), elastomeric polymers

Abstract
Elastomer films with three-dimensional features self-organised into coherent and semi-coherent buckling domains were created by implanting different species of metal ions and combinations thereof, using a metal evaporation ion source, into quality polydimethylsiloxane (PDMS) films. As a result of the implantation process, functionalised discreet regions of strain-induced surface buckling were created, taking the forms of domains of parallel surface waves, semi-ordered regions, and disordered regions. In addition, deep, strain-induced V-shaped cracks were observed to penetrate well into the elastomer matrix. Characterisation was via optical microscopy, x-ray diffraction, atomic force microscopy, and high-resolution secondary electron microscopy (SEM) in the form of field emission SEM. It was found that controlling the localised strain by altering the metal ion species can control the frequency of the V-shaped cracks and the properties of the buckled areas. These observations, as well as possible mechanisms for the formation of the cracks and domains, are discussed in this paper.
Introduction

Polydimethylsiloxane (PDMS) is a commonly used silicon-based organic, cross-linkable elastomer. It is homogeneous, isotropic, and optically transparent down to 300 nm. In its cross-linked state, the elastomer does not permanently deform under stress or strain, and it is stable over a wide temperature range [1]. PDMS is chemically inert, and so the material can be made biocompatible [2] with appropriate chemical and/or physical treatment to enable it to give the desired interfacial interactions. These properties make PDMS desirable for use in the production of numerous active and passive implantation devices that are in direct and sometimes prolonged contact with human tissues [3-4], from artificial lungs [5] to artificial finger joints [6].

As well, the modification of such elastomer surfaces, chemically and topologically, have a variety of scientific and technological applications that range from mechanotransduction, tissue engineering and regenerative medicine based on altering surface topology and controlling the mechanical environment [7-10], and micro-fluidics and lab-on-chip devices [11-12], to memory storage devices [13-14], stretchable electronics, optical diffraction gratings, optical micro lenses [15-16], and biosensors [17-18].

In the field of mechanotransduction, tissue engineering, and regenerative medicine, surface modification is particularly important, since cells are sensitive to all length scales from macro to molecular, and the manipulation of the cell-material interface is critical to controlling and manipulating cellular growth [19-21].

Buckling is an easy ‘bottom up’ way of using a self-organising buckling effect to create and tune different topological structures on the submicron to micrometer scales [22-23]. Recent techniques to create three-dimensional (3D) regular self-organised surface features on the micron and submicron scales via buckling of PDMS surfaces include plasma treatment and oxidation [24-27], metal deposition [28-30], ion beam irradiation [12,22,31], and ionising radiation [32]. This current
work introduces and investigates a new mechanism for producing similar buckling
behaviour to that reported previously for other methods, based on low energy
metal ion implantation past a critical dose.

An advantage of this method over other methods used to buckle the surface of
elastomers is that it results in elementally rich micron-sized features. Previous work
has shown that topography affects the elemental properties [33], as such metal
ions can also be used to introduce desired functional behaviour into the 3D self-
organised surface features. This work has used optically active and magnetic ions in
functionalising these features. A variety of metal ions were used, including Ni, Co,
Fe, and Eu, as well as combinations of them. The magnetic properties of Ni, Co, and
Fe and the optical properties of Eu are widely understood, and this method of
producing buckling results in functionalised 3D surface structures with high
elemental concentrations at the surface. The objective of this study is the creation
and elemental functionalisation of 3D regular, self-organised surface features via
buckling in PDMS via metal ion implantation.

Materials and Methods
A series of identical high quality 4µm thick PDMS films were created by spinning a
liquid silicone mixture with a standard base and catalyst ratio of 10:1 (Sylgard-
184, Dow Corning), onto a (111) single-sided polished silicon wafer (obtained from
Solar Wafers) for 120 s at 8000 rpm. The liquid silicone was allowed to degas for 10
minutes in a cool vacuum oven in order to eliminate the air bubbles introduced
while mixing.

Prior to ion implantation, the surface of the PDMS film was inspected by scanning
electron microscope (SEM) and atomic force microscope (AFM), and its aspect was
smooth, homogeneous, and featureless. These features appear to be stable in time,
as evidenced from inspecting the PDMS film surface over a period of days and
weeks.
The resulting series of unstrained, homogeneous, optically transparent 4 μm films of PDMS on Si wafers were ready for ion implantation carried out using a metal vapour vacuum arc ion source.

For the variety of metal ion species used, Fe, Ni, Co, and Eu, the acceleration voltage and the beam current were kept fixed at 45 kV and 80 mA respectively, but the implantation time varied from 5 s to 20 min. The resulting implanted dose was determined by Rutherford backscattering spectroscopy (RBS) for each implanted ion. At the highest doses, the metal concentration reached 10 at% at the surface. In addition, a number of samples were partially masked during the ion implantation in order to create a transition zone between the implanted and non-implanted areas of the polymer.

Once ion implanted, a number of techniques were used to characterise the modified surfaces of the PDMS thick films. A GBC-MMA diffractometer with thin film attachment and Cu Kα radiation was used for X-ray diffraction (XRD). Both θ - 2θ and the grazing angle were used to analyse the now multi-layered film, with respect to both the composition and the lateral stress in the film with increasing angle of incidence. The composition of the multi-layers was also confirmed using cross-sectional transmission electron microscopy (TEM).

The surface morphology was characterised by AFM (Asylum MF-P3D) in contact mode, optical microscopy, and high-resolution electron microscopy in the form of field emission SEM (FESEM; Joel JSM – 7500FA).

Results
Immediately after the metal ion implantation was carried out, the surface of the polymer irradiated by the ion flux became altered and covered by what appear to be stress-induced V-shaped cracks or cracks that penetrate deeply into the elastomer matrix (Fig. 1). It is well known and has been demonstrated that V-shaped cracks tend to open up on the surface as a method of strain relief [34], thus,
as expected, the frequency of these V-shaped cracks increases with implantation dose. Also, as will be detailed later, metal ion species that induce greater strain into the elastomer matrix increase the frequency of occurrence of the V-shaped cracks.

Figure 1 shows the AFM and cross-sectional analysis of a crack, with the strain-relief induced V-shaped cracks being approximately 2μm in depth, penetrating deeply into the elastomer matrix. It was found that increasing the surface damage through increased dose and/or the use of more damaging ions increased the crack depth.

Figure 1: Typical AFM scan of a characteristic heat induced surface crack. Note the V-shape, indicating a strain induced feature.
Over time, a wave-like regular pattern, as seen in the AFM images in Fig. 2, completely covers the surface of the film and fills in the space between the surface cracks. The time required for the regular buckling pattern to appear was governed by the implanted metal ion species and ranged from nearly instantaneous to several hours. This represents a new mechanism for creating and controlling buckling on the surface of PDMS.

The implantation of metals into the surface of PDMS, past a critical dose, thus serves to deliver results comparable to those observed by Bowden et al. [24, 28]. Due to its stability, this behaviour would not spontaneously occur without modification of the PDMS surface, and TEM results show that the elastomer matrix remains well adhered to both the silicon support wafer and the damaged surface layer.
Figure 2: Sectional AFM scan of the characteristic sine function-like ripples that appear after ion implantation. Different metal ion species result in altered frequency and amplitude of the buckles.

AFM was also conducted in contact mode on partially covered films (Fig. 3), demonstrating the clear transition between the implanted and un-implanted surface behaviour. The covered film remained smooth, homogeneous, and optically transparent, as expected, while the exposed region of the film showed damage to the PDMS surface in the form of large V-shaped cracks, as seen in Figure 1 in an AFM sectional scan, and in the buckling that develops over time, as seen in Figure 2. Both the surface and the cross-sectional analysis of a partially covered film are displayed.
Visible undulations appear, even for relatively short periods of exposure of seconds to tens of seconds, with the critical dose dictated by which metal species is being implanted. This characteristic buckling dominates the surface, and cross-sectional analysis shows the buckles to be remarkably sine wave-like, with an amplitude of just over 1 micron. The amplitude and frequency of these features can be controlled through the accelerating voltage, fluence, and current of the ion beam or the metal ion species. It is implied that altering these parameters affects the thickness of the stiff film by altering the penetration depth of the metal ions [21-22]. The AFM and optical microscopy showed similar buckling behaviour in all films,
independent of the ion species implanted. What differed was the amplitude and frequency of the surface ripples and the depth and frequency of the stress induced cracks, which were influenced by the dose of implanted metal ions.

To track the evolution of the buckling process with increasing dose, films were exposed to very small doses, which were gradually increased (Fig. 4). As the implantation doses increased, the frequency of the V-shaped cracks, the wavelengths of the buckles, and the density of buckling increased until reaching a saturation point, after which no further increase in buckling density was seen.

Figure 4: The evolution of the buckling effect with dose, with a) 5 s of Fe implantation, b) 25 s of Fe implantation, and c) 3 min of Fe implantation. The white area outside the buckling is the unmodified film.

The V-shaped pits, defects, voids, dust particles, and even edges on the surface served as initiation sites for the buckling, which upon higher doses quickly branches out to completely cover the surface of the exposed films in a semi-chaotic pattern of herringbone ripples.

To further investigate the surface buckling process, optical microscopy was used to examine a wider area of the PDMS film surface, and the results are shown in Figure 5. Because buckling is also a stress related phenomenon, and any stress is relieved at the V-shaped cracks on the surface, any buckling becomes ordered perpendicular to these cracks. Away from the V-shaped cracks, the buckling becomes disordered and forms a multitude of partial domains.
The RBS results discussed earlier confirmed a silicon and oxygen rich layer at the surface of all the ion-implanted films, to varying degrees. The long-range atomic order was probed with grazing angle XRD for both the silicon rich layer and the elastomer matrix for the films implanted with different metal ion species. The results for Ni implanted PDMS are shown in Fig. 6. All metal species and other various combinations of implanted ions displayed similar patterns. To further investigate, the surface of a thick polydimethylsiloxane (PDMS) film was modified with different metal ions and/or a combination using metal ion implantation techniques. X-ray diffraction gives evidence that the implantation process quickly
forms, through chain-scission, large highly textured surface crystals of silica at the surface of a stiff silicon and oxygen rich layer that adheres to the elastomer base, where the thickness and the concentration of silicon depend on the penetration depth and dose of the implanted ions. Controlling the accelerating voltage and fluence or current of the ion beam can further influence the formation of this silicon and oxygen rich film.

In addition, low incident angle scans were done at a number of angles of incidence to investigate the stress-strain mismatch between the multi-layers and the internal stress of the stiff silicon rich layer, as well as the different strain properties of different types of metal ion implantation. The grazing angle scans included high intensity, narrow peaks, consistent with the formation of thin textured silicate crystals on the surface. Such crystallisation might be the result of oxidation and subsequent decomposition. As expected, the surface features ensure that changing the incident angle results in different silica peaks at different relative intensities.

The characteristic broad peak between 10 and 15 degrees, corresponding to the diffraction of tiny crystals of PDMS, also shows a very slight shift to the left, confirming the internal stress in the elastomer matrix as a consequence of the multi-layers [35].
Figure 6: Grazing angle XRD of Ni implanted PDMS thick film, with implantation carried out for 15min (~17,000 shots). The increasing angle of incidence shows the strain induced peak shifts.

The high resolution SEM aspect of the surface presented in Fig. 7 shows nanosized holes, suggesting the possible evolution of a gaseous phase from the top layer of the film, consistent with the formation of methane. This is an indication that the energy delivered by the implanting ions leads to the decomposition of the surface. Chenoweth et al. [36] demonstrated that at temperatures above 900 K and with a fast heating rate, degradation of PDMS occurs through a radical mechanism involving Si-CH$_3$ homolytic bond cleavage, followed by hydrogen abstraction to form methane [37-38], leaving a silicon rich layer. This is further evidence of structural modification in the top layer.
Figure 7: Surface porosity of the decomposed PDMS layer after ion implantation.

As shown by the peak shifts in Fig. 6 and as summarised in Table 1, the mechanical differences between the adhered silica rich stiff skin and the elastomer matrix lead to a lateral force mismatch, resulting in surface undulations in the form of buckles as the silicon and oxygen rich layer undergoes compressive stress. To accommodate the induced mismatch strain between the skin and the elastomer substrate, the skin buckles in a wave-like manner, with wavelengths that are much larger than the stiff skin thickness and smaller than the overall dimensions of the elastomer base.
Table 1: Shift in broad PDMS peak as a result of surface strain.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Composition</th>
<th>Peak Position in Grazing Angle Scan (°)</th>
<th>3° Grazing Angle</th>
<th>9° Grazing Angle</th>
<th>Strain Shift (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>Ni</td>
<td></td>
<td>11.67</td>
<td>12.2</td>
<td>0.53</td>
</tr>
<tr>
<td>E</td>
<td>Ni, Fe</td>
<td></td>
<td>11.59</td>
<td>12.43</td>
<td>0.84</td>
</tr>
<tr>
<td>F</td>
<td>Ni, Eu</td>
<td></td>
<td>11.67</td>
<td>11.98</td>
<td>0.31</td>
</tr>
</tbody>
</table>

Table 1 shows the effects on the internal stress of Ni implantation and the implantation of two combinations of ions. Lower strain shift led to a decreased frequency of stress relieving V-shaped pits, suggesting a method of further control over the formation of functionalised self-organising 3D surface features.

**Conclusions**

In this work, the chemical composition and strain of the surface layers of the modified PDMS thick films have been investigated, as well as the surface buckling morphology. We have successfully shown that ion implantation can be used to modify the surface of PDMS by inducing buckling through the decomposition of the surface of a PDMS thick film. Metal ion implantation causes significant internal stress within this stiff upper layer, which causes V-shaped cracks to form randomly, with an ordering of the buckling around these points. The buckling is disordered away from any V-shaped cracks, forming partial domains.

We have also shown that the internal stress can also be controlled through not just dose, but by using a variety of metal ions, thus allowing for higher concentrations of functional metal ions. Work on further characterising and controlling the cracks and buckles with varying doses and ions, and combinations of ions is ongoing.
References

Buckling Induced Patterns in Thin Confined Elastic Films by Ion Implantation

B. R. Winton\textsuperscript{a}, M. Ionescu\textsuperscript{b}, and S. X. Dou\textsuperscript{a}

\textsuperscript{a} ISEM, University of Wollongong.
\textsuperscript{b} Australian Nuclear Science and Technology Organisation.

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Low energy metal ion implantation has been used to combine an easy ‘bottom up’ way of creating and tuning different topographic structures on submicron to micrometer scales with the embedding of a metallic element-rich functionalised layer at the surface for a variety of scientific and technological applications. The self-organising and complex patterns of functionalised topographic structures are highly dependent on the implanted metal ion species, variations in the geometric confinement of the buckled areas on the larger unmodified elastomer film, and the boundary conditions of the buckled regions. Systematic investigations of these dependencies have been carried out via optical and atomic force microscopy, and confirmed with cross-sectional transmission electron microscopy.

Introduction

Polydimethylsiloxane (PDMS) is a commonly used silicon-based, organic, cross-linkable elastomer. It is homogeneous, isotropic, and optically transparent down to 300 nm. In its cross-linked state, the elastomer does not permanently deform under stress or strain, and it is stable over a wide temperature range \[1\]. PDMS is chemically inert, and thus the material can be made biocompatible \[2\] with appropriate chemical and/or physical treatment to enable it to give the desired interfacial interactions. These properties make PDMS attractive for use in a variety of scientific and technological applications including: microfluidics and lab-on-chip devices \[3-4\], memory storage devices \[5-6\], stretchable electronics; smart adhesives \[7\], optical diffraction gratings; optical microlenses \[8-9\], and biosensors \[10-13\].
ease with which dominant and complex patterns can be generated and controlled on the surface of an elastomer film makes self-organising buckling an easy ‘bottom up’ way of creating and tuning different topographic structures on submicron to micrometer scales for such applications.

As well as for its usefulness in controlling the topographical regimes of buckling, metal ion implantation was chosen because it can also further functionalise the surface. Previous work has found that combining magnetic materials with wrinkling of PDMS can lead to magnetic correlations within the range of the buckling features \[12\]. This has led to the creation of ferroscaffolds with unique topographical formations, which hold enormous potential as stimulus-responsive drug carriers and scaffolding materials for tissue engineering. Hu et al. found that the magnetic sensitivity of ferroscaffolds exhibited different degrees of magnetism, which could be further used to control growth factors for cells cultures \[13\]. Similar behaviour within the range of the buckling features can be expected when combining surface buckling with elemental functionalisation through metal ion implantation.

Surface buckling or wrinkling of the elastomer PDMS can be created in a number of different ways. These include plasma treatment and oxidation \[14-17\], metal deposition \[18-20\], ion beam irradiation \[4, 21\], and ionising radiation \[22\]. The control or tuning of the resultant buckling from these techniques has been achieved through controlling the properties used to induce buckling \[23-24\], pre-patterning the elastomer film \[14, 18, 25\], the use of masks \[15, 21, 26\], or by selectively controlling the thickness of the film \[16\].

In previous work, we have shown that modification of the surface of a thick PDMS film with implanted metal ions can induce complex buckling patterns, while also elementally functionalising the surface features \[27\]. Briefly, Rutherford backscattering spectroscopy (RBS) and grazing angle x-ray diffraction (XRD) conducted earlier confirmed that films exposed to metal ion implantation all have a silicon and oxygen rich layer at the surface, resulting from decomposition of the elastomer, down to varying thicknesses, depending on the dose and the metal ion
species. This leads to the surface becoming covered by stress-induced V-shaped cracks that penetrate deeply into the elastomer matrix. Over time, a wave-like regular pattern completely covers the surface of the film, filling in the space between the surface cracks. This leads to the advantageous situation of having element-rich, functionalised, tuneable, three-dimensional (3D) surface features.

To be useful for applications, however, the functionalised, self-organised, coherent and semi-coherent 3D surface features would need to be selectively induced onto the surface of the elastomer film. In this work, we have conducted a parameter study of this combined method of buckling and functionalisation, to understand the influence of various metal ion species, the varying geometric confinement of buckled areas on a larger unmodified elastomer film, and the boundary conditions imposed by the said geometric confinement on the induced buckling regimes, thereby creating a simple non-photolithographic means of patterning soft materials.

**Experimental**

To study the dependence of the complex buckling regimes on several parameters, such as metal ion species, geometric confinement, and mask boundary conditions, which are integral to the usefulness of metal ion implantation for the purposes of patterning soft materials, a series of identical high quality PDMS 4 \( \mu \text{m} \) thick films was created. This was done by spinning a liquid silicone mixture with a base and catalyst ratio of 20:1 (Sylgard-184, Dow Corning) onto a (111) single-side-polished silicon wafer (obtained from Solar Wafers) for 120 s at 8000 rpm. Before coating, the liquid silicone was allowed to degas for 10 minutes in a cool vacuum oven in order to eliminate the air bubbles introduced while mixing.

The resulting series of homogeneous, optically transparent films of PDMS on Si wafers were then ready for metal ion implantation, which was carried out at room temperature, using a metal vapour vacuum arc ion source. Fe, Co, Au, and Ta were chosen for their variety of atomic weights and oxidising properties. For each sample
produced, the ion acceleration voltage and the beam current were kept fixed at 45 kV and 8 mA, respectively, and several implantation times were used from 5 s to 20 min to determine the effects of controlling the dose on the sigmoidal-like buckling behaviour. Eu, Mg, Ni, and Ti were also implanted at both high and low doses to further confirm universality in the behaviour of implanted metal ion species.

Two aluminium masks with varying sized islands in varying proximity to each other were chosen. The first simply had a linear series of islands of different sizes at a set distance apart (measured from the edges of the islands). However, the second more complex mask had different sized islands at varying distances from each other. This allowed the investigation of edge and proximity effects on buckling behaviour.

The ion implantation parameters were monitored by He RBS, and the surface morphology was characterised by atomic force microscopy (AFM; Asylum MF-P3D) in contact mode and by optical microscopy. Transmission electron microscopy (TEM) was conducted to establish a likely mechanism for the variation in buckling behaviour.

**Results and Discussion**

Immediately following the metal ion implantation of the surface, the PDMS surface became altered and covered by what appeared to be stress induced V-shaped cracks, which penetrated deeply into the elastomer matrix. It is well known and has been demonstrated that V-shaped cracks tend to open up on the surface as a method of strain relief, and the frequency of these V-shaped cracks increases with the strain induced by increased implantation dose \(^{27}\). Over time, a wave-like regular pattern of undulations appears that is divided into complex coherent and semi-coherent domains of various sizes and shapes. These different domains are due to the patterns established by the interference of the differing orientations of the waves that were formed (Fig. 1(a)). These wrinkling domains completely cover the surface of the film and fill in the space between the surface cracks. A domain
boundary was imaged by AFM and is shown in Fig 1(b), supporting the cross-sectional TEM results in showing no evidence of delamination, simply the intersection of stress wave fronts, which produces an optical illusion of height changes. This becomes useful when designing or controlling discrete strain regions for use in technological and scientific applications, since it means that the stiff layer remains coupled to the underlying elastomer base, thereby retaining the bulk elastomer properties of PDMS.

Figure 1: AFM across the intersection of strain induced buckling patterns: a) optical microscope image showing the region of interest, b) AFM scan across an intersection of strain wave fronts, in this case the corner of a polygon. This result is repeated across all intersections, and there is no evidence of delamination occurring.

The time required for these complex, coherent and semi-coherent buckling domain patterns to appear was governed by the implanted metal ion species and ranged from nearly instantaneous to a period of several hours. A qualitative analysis of the time dependence of wrinkle pattern formation for the metal ions implanted suggests the cause. When an energetic ion impacts the surface of the elastomer, the structure and composition are irreversibly changed, primarily through chain scission into lower molecular weight chains and the release of volatile species, to a depth that depends on the mass of the implanted metal ion and its energy. At the same implantation energy, the more massive an implanted ion is, the less it will
penetrate into the material and the narrower the Gaussian profile of implantation will be, due to the way in which the energetic ion loses energy in the solid matrix, mostly through interaction with the electrons of the target. This leads to variations in the depth and thickness of the metal rich layer implanted into the polymer matrix.

Cross-sectional TEM (Fig. 2) shows that, at the ion implantation potential used in this work, the range of implanted ions agrees with a TRIM calculation of a Gaussian depth distribution, with the peak at around 40 nm, and this was further confirmed by He RBS. However, from the TEM cross-sectional images shown in Fig. 2, it appears that there are varying and distinct compositional layers in the polymer as a result of the implantation, down to around 250 nm. This modification of the polymer matrix is deeper than the implantation depth of the metal ions. It has been speculated that this is due to further complex interactions between the polymer matrix and the energetic ions. This phenomenon requires further attention, and it is currently under investigation.

Figure 2: Cross-sectional TEM images of PDMS irradiated with Ni, Fe, and Au for 20 min, using an accelerating voltage of 50 kV and a beam current of approx. 1 mA. The black region is a metal coating grown on the surface as part of the focused ion beam (FIB) lift out process.

After the implantation process, the lower molecular weight molecules (LMW) will diffuse up to the surface from the elastomer bulk over time. The diffusion time is influenced by both the thickness of the surface layer, thinner layers lead to shorter diffusion times due to a smaller volume to serve as the LMW repository, and also the thickness of the metal rich layer acting as a barrier to diffusion. This explains
then why the gold implanted surface formed wrinkles within seconds, followed by iron, nickel, and cobalt, with titanium and magnesium taking the longest. Gold ions are more massive and so penetrate less deeply, creating a thinner stiff surface layer and also a thinner metal rich layer to act as a barrier for the LMW molecules.

![Optical microscope image of a geometrically confined region of buckling. Exposure time is 30 s.](image)

Geometric confinement also plays a role in controlling the wavelength of the sine-wave-like buckles within the islands. With the use of an Al mask, islands of buckling were induced onto a larger PDMS thick film confined on a Si wafer. There was an approximately constant 3 \( \mu m \) increase, for all metal ions tested, in the wavelength recorded between the buckling at the centre of the island and that at the edge of the island. This suggests that there is a radial strain that increases linearly from the centre of the island to the edge as a result of the use of a mask. This 3 \( \mu m \) increase
in buckling wavelength was consistent for all island sizes tested, so we can treat the implantation process as homogeneous across the islands, ruling out any gradient effect resulting from the metal ion implantation.

This persistence of the aligned radial buckling at the edge of the island is due to the azimuthal strain from the implanted ions, which is induced by circumferential pressurization at the boundary due to the unmodified PDMS elastomer and the modulus mismatch \(^{[30-31]}\). This leads to increases in the length of the aligned radial buckling at the edge of the island with dose, but decreases in the length with increased island size.

In the interior of the implanted islands, away from the geometrically confined, radially aligned buckling, random self-organised coherent and semi-coherent buckling morphologies are seen to form. As the strain increases, the morphologies undergo a transition from radial and hooping zigzag patterns, to “telephone cord” buckling. This leads to a pattern of polygons in spots where random buckling intersects (Fig. 3). While the wavelength of the wrinkling is dependent on the metal ion species, as discussed, the wrinkling morphologies resulting from strain are similar in all cases.

Unmentioned so far, has been the possibility of using a shadowing effect from the ion implantation to create useful morphologies. Through clever mask design, the shadowing effect resulting from the distance of the mask from the film allows a small area immediately outside the island to receive a fraction of the dose of the exposed island. This allows the creation of specific strain minimisation effects outside the buckled island, dependent on the dose and radius of curvature of the island boundary, which results in a buckling morphology that is significantly different from that inside the island.

Figure 4 shows boundary conditions resulting from two different radii of curvature, which have led to entirely different morphologies in islands implanted with
identical doses of Fe. The edges of the islands with the two radii of curvature (Fig. 4) also highlight the evolution of the edge effect outside the boundary of the buckled island, with the first panel (Fig 4(a)) showing a large radius of curvature, with an island size of 5 mm, giving the impression of an almost straight line at the given scale, and the second panel showing a smaller radius of curvature (Fig. 4(b)), with an island size of 1 mm, which at the same scale appears discontinuous. Figure 4 also serves to highlight the evolution of buckling with increasing strain. There are three regions of strain clearly delineated, and this behaviour is similar for all island sizes and metal ion species: the first 20 \( \mu \text{m} \) closest to the edge, followed by a different alignment for another 80 \( \mu \text{m} \) out, followed by random buckling. Using these relationships, and by regulating the dose and the curvature of the boundary through island size, different buckling regimes of determinable length, both with and without the island, can be manufactured as part of a larger scale buckled system, where a variety of buckling regimes are needed within a single system. Usefully, the shadowing effect can be further controlled when two shadowing effects are placed in proximity. An approximately 50 \( \mu \text{m} \) wide field of 2 \( \mu \text{m} \) buckles has been established that is an order of magnitude smaller than the buckling seen in the exposed island region.
Figure 4: Optical microscope images of two different radius of curvature boundary conditions, for identical dose of Fe implantation, resulting in different strain buckling: a) large radius of curvature (island radius 5 mm) leading to three distinct regions of strain at the outside of the implanted island; b) small radius of curvature (island radius 1 mm) with lower strain, showing the beginning of the buckling edge effects; c) and d) AFM results from across the edge of the larger and smaller metal ion implanted islands, respectively.

Initially, wrinkling was induced onto an unstrained, unconfined PDMS film to demonstrate the effects of low energy implantation of various metal ions at different doses. All of the implanted ions behaved similarly with dose, with the wavelength of the wrinkles rapidly increasing with increasing dose until a critical dose at which the increases in wavelength started levelling off in a sigmoidal-like behaviour, as seen in Figure 5. The various ions start buckling at dramatically different wavelengths, which leads to a levelling off with time at different ranges, where with constant dose, the wavelength of the sine-like buckling pattern was found to be dependent on the metal ion species implanted. Since all implanted metal ions behave similarly in inducing wrinkling, albeit with different wavelengths, results for iron implanted PDMS are shown hereafter for consistency.
While it has already been shown that low energy ion implantation acts to decompose the surface of the elastomer to a silicon and oxygen rich stiff layer, thereby causing the wrinkling behaviour due to strain mismatch \cite{27}, this does not explain the difference in the sigmoidal-like behaviour shown when different metal ions are implanted. It is speculated that the dependence of the PDMS wrinkle wavelength on the metal ion species is due to a metal rich layer implanted into the elastomer matrix. Once implanted, the metal ions act to form either a homogeneous metal-rich oxide composite layer or a layer of metallic clusters suspended within the elastomer matrix beneath the decomposed stiff layer. The thickness and depth of this metal-rich layer is dependent on the dose and penetration depth of the metal ions implanted. This conclusion is supported by previous work done on metal ion implantation in polyethylene terephthalate. \cite{32, 33}. Earlier glancing angle XRD results, which showed that different ion species introduced different amounts of strain into the surface layer, along with initial cross-sectional TEM of Ni, Fe, and Au implanted PDMS, demonstrate that various depths and thicknesses of metallic rich layers could affect the wavelength. Unlike Fe, Co, and Ta, Au only has 3 data points, so it is possible that the trend may be dissimilar, although the authors think this unlikely.
Since all of these parameters are fairly easy to control, a combination of geometric confinement through the clever selection of masks, dose, and metal ion species would allow the engineering of several different buckling regimes, with different elemental functionalisation of 3D features within a global buckling system. This constitutes a large advantage of this method of buckling for easy ‘bottom up’ creation and tuning of different topological structures on submicron to micrometer scales for use in a variety of scientific and technological applications.

Conclusion

We have successfully shown that low energy metal ion implantation can be used to modify the surface of PDMS into different functionalised buckling morphologies, within a global system of buckling, by inducing and directing discreet regions of strain without the effort of pre-patterning the substrate. This is done through the control of the metal ion species, the dose, and the geometric confinement of the buckled area and control of the boundary conditions by the use of masks. This
allows for a rapid and versatile ‘bottom up’ way in which to create discrete
topological morphologies for use in the selective modification and control of the
surface topology of elastomers for future applications such as degradable
biomedical devices, including surgical dressings, vascular grafts, tissue engineering
scaffolds, sutures, and structures for guided tissue regeneration.
References
Micro-patterned Surface modification of Poly(dimethylsiloxane) (PDMS) substrates for Tissue Engineering

Brad R. Winton\textsuperscript{a)}, Mihail Ionescu\textsuperscript{b)}, Chris Lukey\textsuperscript{c)}, Mark Wilson\textsuperscript{d)}, Ivan P. Nevirkovets\textsuperscript{a)}, Shi X. Dou\textsuperscript{a)}

Please see print copy for the article on page 220-239

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