Catalytic Silane Nanopatterning using Scandium Triflate Functionalised PPL Arrays

A dissertation submitted to the University of Manchester for the degree of Master of Chemistry by Research in the Faculty of Science and Engineering

2017

David T. Arrowsmith
School of Chemistry
# Table of Contents

Title Page ....................................................................................................................................... 1

Table of Contents .......................................................................................................................... 2

Word Count .................................................................................................................................... 4

List of Figures ................................................................................................................................ 5

List of Schemes ............................................................................................................................. 7

List of Tables ................................................................................................................................. 8

List of Abbreviations ...................................................................................................................... 9

Abstract ........................................................................................................................................ 11

Declaration ................................................................................................................................... 13

Copyright Statement .................................................................................................................... 13

Acknowledgements ...................................................................................................................... 14

1. Introduction ............................................................................................................................. 15

1.1. Rare Earth Metal Triflates as Water Tolerant Lewis Acid Catalysts ................................. 15

1.2 Scandium Triflate as a Lewis Acid Catalyst in the Silylation of Silanols ............................ 18

1.3. Scandium Triflate Localisation on Solid Supports ............................................................ 21

1.4. Dip Pen Nanolithography ................................................................................................. 22

1.5. Polymer Pen Lithography ................................................................................................. 23

1.6. Catalytic Nanolithography ............................................................................................... 25

2. Aims ......................................................................................................................................... 27

3. Scandium Triflate Catalysed Nanolithography of Methallylsilanes on Oxidised Substrates ... 30
6.3. Analysis ............................................................................................................................ 59

6.3.1. XPS ........................................................................................................................... 59

6.3.2. AFM ........................................................................................................................... 60

6.3.3. CAG .......................................................................................................................... 60

6.3.4. GCMS ....................................................................................................................... 61

6.3.5. Catalytic Activity Test of Substrate E ........................................................................ 61

6.4. Molecular Sc(OTf)$_3$ Nanolithography Methods ................................................................. 62

6.4.1. General Procedures .................................................................................................. 62

6.4.2. PPL of DTMS on Oxidised Silicon ............................................................................ 63

6.5. Surface Functionalisation Methods for R-Sc(OTf)$_2$ Localisation ................................. 63

6.5.1. Substrate A ............................................................................................................... 63

6.5.2. Substrate B ............................................................................................................... 64

6.5.3. Substrate C ............................................................................................................... 65

6.5.4. Substrate D ............................................................................................................... 65

6.5.5. Substrate E ............................................................................................................... 66

6.5.6. Functionalisation of PPL Arrays ................................................................................ 66

References .................................................................................................................................. 67

Word Count: 10192
List of Figures

Figure 1. Bonding modes of triethoxysilanes and dimethallylsilanes at an oxidised silicon surface.......................................................................................................................................................................................... 20

Figure 2. Stylised depiction of a DPN procedure ................................................................................................................................. 23

Figure 3. Polymer pen lithography ......................................................................................................................................................... 24

Figure 4. A schematic illustration of catalytic scanning probe lithography .......................................................................................... 26

Figure 5. A representative schematic illustrating catalytic PPL of trimethallylsilanes on to oxidised silicon using a molecular Sc(OTf)₃ catalyst deposited on the substrate surface.............. 28

Figure 6. A representative schematic illustrating catalytic PPL of trimethallylsilanes on to oxidised silicon using a scandium triflate catalyst bound to the PPL array ........................................ 29

Figure 7. Optical microscope images of Sc(OTf)₃ spin-coated oxidised silicon substrates........... 32

Figure 8. XPS spectra of four 300x700µm areas on the surface of an oxidised and Sc(OTf)₃ spin-coated silicon wafer.................................................................................................................................................. 33

Figure 9. LF-AFM image of features produced by PPL of DTMS on a Sc(OTf)₃ spin-coated oxidised silicon substrate with 30% humidity, 3µN contact force and dwell times of 1s to 30s... 35

Figure 10. LF-AFM images of features produced by PPL of DTMS on a Sc(OTf)₃ spin-coated oxidised silicon substrate with 15% humidity, 1µN contact force and dwell times of 750ms to 100ms.................................................................................................................................................. 36

Figure 11. XPS spectra of substrate C ................................................................................................................................. 48

Figure 12. XPS spectra of substrate D ................................................................................................................................. 49

Figure 13. Catalytic activity test results ................................................................................................................................................ 51

Figure 14. PPL master dimensions ................................................................................................................................................ 57
Figure 15. Apparatus setup for the catalytic activity test of substrate E...............................62

Figure 16. Apparatus setup for application of reagent solutions to substrates .........................65
List of Schemes

Scheme 1. The Mukaiyama aldol reaction of (Z)-1-phenyl-1-(trimethylsiloxy)propene with benzaldehyde ...................................................................................................................................................... 16

Scheme 2. Hydroxymethylation of a generic silyl enol ether in aqueous media by catalysis with Yb(OTf)₃ ......................................................................................................................................................... 18

Scheme 3. General siloxane synthesis by reaction of an alcohol with t-butyldimethyl(2-methallyl) silane ....................................................................................................................................................... 19

Scheme 4. Functionalisation of an oxidised silicon substrate by Sc(OTf)₃ catalysed silylation with a methyl(di(methallyl))silane .................................................................................................................................................. 19

Scheme 5. Preparation of a scandium catalyst localised on polystyrene supports via an alkylaromatic linker ..................................................................................................................................................... 22

Scheme 6. Sc(OTf)₃ catalysed silylation of an oxidised silicon substrate with dodecyltri(2-methallyl) silane ...................................................................................................................................................... 30

Scheme 7. Functionalisation of an oxidised silicon substrate surface with an alkylsulfonic acid moiety ....................................................................................................................................................... 42

Scheme 8. Conversion of a sulfonic acid functionalised substrate to a scandium triflate functionalised substrate by reaction with ScCl₃ followed by TfOH ........................................................................................................ 42

Scheme 9. Conversion of a sulfonic acid functionalised substrate to a scandium triflate functionalised substrate by direct reaction with Sc(OTf)₃ .................................................................................................................................................. 43

Scheme 10. Proposed scheme for the catalytic activity test of substrate E .................................................................................................................................................................................. 51
List of Tables

Table 1. Comparison of the pKₐ and WERC of various metal cations, and the catalytic activity of derived Lewis acids in the Mukaiyama aldol reaction of benzaldehyde with (Z)-1-phenyl-1-(trimethylsiloxy)propene ............................................................. 17

Table 2. Conditions used for polymer pen lithography of DTMS on Sc(OTf)₃ dip-coated oxidised silicon substrates ......................................................................................................................... 31

Table 3. Conditions used for polymer pen lithography of DTMS on Sc(OTf)₃ spin-coated oxidised silicon substrates ........................................................................................................... 34

Table 4. Control lithography experiments .................................................................................... 38

Table 5. Water contact angles of functionalised silicon substrates by water contact angle goniometry ................................................................................................................................... 44

Table 6. XPS analysis of oxidised and un-oxidised silicon wafer, and substrates A to E ............ 46

Table 7. XPS parameters (K-Alpha, NEXUS, University of Newcastle) .............................................. 59

Table 8. XPS parameters (Axis Ultra Hybrid, University of Manchester) ........................................... 60

Table 9. GCMS conditions ........................................................................................................... 61
## List of Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>3-MPTMS</td>
<td>3-mercaptopropyltrimethoxysilane</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
</tr>
<tr>
<td>ATR-IR</td>
<td>Attenuated total reflection infrared spectroscopy</td>
</tr>
<tr>
<td>CAG</td>
<td>Contact angle goniometry</td>
</tr>
<tr>
<td>CP-MAS NMR</td>
<td>Cross-polarisation magic angle spinning nuclear magnetic resonance spectroscopy</td>
</tr>
<tr>
<td>DPN</td>
<td>Dip-pen nanolithography</td>
</tr>
<tr>
<td>DTMS</td>
<td>Dodecyltris(2-methallyl)silane</td>
</tr>
<tr>
<td>EWG</td>
<td>Electron withdrawing group</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>FWHM</td>
<td>Full width at half maximum</td>
</tr>
<tr>
<td>$K_h$</td>
<td>Hydrolysis constant</td>
</tr>
<tr>
<td>LF-AFM</td>
<td>Lateral force atomic force microscopy</td>
</tr>
<tr>
<td>MATS</td>
<td>(Methallyl)trimethylsilane</td>
</tr>
<tr>
<td>NMR</td>
<td>Nuclear magnetic resonance spectroscopy</td>
</tr>
<tr>
<td>Oxone®</td>
<td>Potassium peroxymonosulfate</td>
</tr>
<tr>
<td>PDMS</td>
<td>Polydimethylsiloxane</td>
</tr>
<tr>
<td>PPL</td>
<td>Polymer pen lithography</td>
</tr>
<tr>
<td>R-Sc(OTf)$_2$</td>
<td>Scandium triflate (localised)</td>
</tr>
<tr>
<td>SAM</td>
<td>Self-assembled monolayer</td>
</tr>
<tr>
<td>Sc(OTf)$_3$</td>
<td>Scandium Triflate</td>
</tr>
<tr>
<td>SIMS</td>
<td>Secondary ion mass spectrometry</td>
</tr>
<tr>
<td>TES</td>
<td>Tetraethylsilanol</td>
</tr>
<tr>
<td>Tf</td>
<td>Trifluoromethanesulfonate, Triflate</td>
</tr>
<tr>
<td>THF</td>
<td>Tetrahydrofuran</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Description</td>
</tr>
<tr>
<td>--------------</td>
<td>-------------</td>
</tr>
<tr>
<td>TIPS</td>
<td>Triisopropylsilanol</td>
</tr>
<tr>
<td>TTDS</td>
<td>1,1,1-triisopropyl-3,3,3-trimethyldisiloxane</td>
</tr>
<tr>
<td>WERC</td>
<td>Water exchange rate constant</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
</tbody>
</table>
Abstract

Nanolithography describes procedures for the production of nanoscale features (<100nm) on surfaces by removal (top-down nanofabrication) or deposition (bottom-up nanofabrication) of material. Such procedures have broad applications in nanodevice production. Current methods for bottom-up nanolithography of covalently bound compounds on silicon substrates generally require pre-functionalisation of the surface, for example by deposition of organic species or coating with a suitable metal. While these approaches permit effective lithographic generation of a wide range of surface functionalities, pre-functionalisation requires specialist equipment or use of water sensitive chemicals that may be prone to self-polymerise, necessitating careful control of conditions to ensure formation of regular surface structures. A simple and effective procedure for direct lithography of organic species on to oxidised silicon to generate covalently attached chemical features would simplify surface nanofabrication by reducing the need for such technical pre-treatments.

This work examines an approach to that end. Scandium triflate is a water-stable Lewis acid that demonstrates high catalytic activity in a variety of traditional Lewis acid catalysed reactions. A procedure for the covalent functionalisation of oxidised silicon substrates with methallylsilanes using catalytic scandium triflate has been demonstrated. The reagents used in these procedures are typically stable in the presence of water and in the absence of a Lewis acid catalyst, enhancing control of their reactivity.

This dissertation explores means of adapting this chemistry to nanolithographic protocols to permit direct lithography of methallylsilane-derived features on to oxidised silicon substrates. Two approaches were adopted to this end.
First, molecular scandium triflate was used in procedures for dip-pen polymer pen lithography of dodecyltris(2-methallyl)silane on oxidised silicon. Features of $2.5\pm0.28 \, \mu m$ were successfully generated with good reliability and repeatability. Smaller features of $439\pm70 \, nm$ were produced with reduced but moderate reliability.

Second, attempts were made to tether a scandium triflate catalyst to a PDMS polymer pen lithography array to permit its repeated use in nanolithography. Functionalisation protocols were developed and tested on silicon substrates. Contact angle goniometry and x-ray photoelectron spectroscopy evidenced functional changes at the substrate surfaces including the presence of scandium in certain cases. Further attempts to characterise the surface yielded poor results. One of the functionalisation protocols was performed on PPL arrays. These were used in attempts to perform catalytic nanolithography of dodecyltris(2-methallyl)silane on to oxidised silicon substrates. Lithography features detectable by atomic force microscopy were not successfully generated. Further work in this area is required.
Declaration

No portion of the work referred to in the dissertation has been submitted in support of an application for another degree or qualification of this or any other university or other institute of learning.

Copyright Statement

i. The author of this dissertation (including any appendices and/or schedules to this dissertation) owns certain copyright or related rights in it (the “Copyright”) and s/he has given The University of Manchester certain rights to use such Copyright, including for administrative purposes.

ii. Copies of this dissertation, either in full or in extracts and whether in hard or electronic copy, may be made only in accordance with the Copyright, Designs and Patents Act 1988 (as amended) and regulations issued under it or, where appropriate, in accordance with licensing agreements which the University has from time to time. This page must form part of any such copies made.

iii. The ownership of certain Copyright, patents, designs, trademarks and other intellectual property (the “Intellectual Property”) and any reproductions of copyright works in the dissertation, for example graphs and tables (“Reproductions”), which may be described in this dissertation, may not be owned by the author and may be owned by third parties. Such Intellectual Property and Reproductions can not and must not be made available for use without the prior written permission of the owner(s) of the relevant Intellectual Property and/or Reproductions.

iv. Further information on the conditions under which disclosure, publication and commercialisation of this dissertation, the Copyright and any Intellectual Property and/or Reproductions described in it may take place is available in the University IP Policy, in any relevant Dissertation restriction declarations deposited in the University Library, The University Library’s regulations and in The University’s policy on Presentation of Dissertations.
Acknowledgements

I would like to thank my primary supervisor Dr. Lu Shin Wong for his advice, support and encouragement over the course of my project and for providing me with the opportunity to undertake this work.

I would like to thank Dr. Ben Spencer of the University of Manchester and also staff at the EPSRC NEXUS facility at the University of Newcastle for performing XPS analysis of samples on my behalf.

For demonstrating the AFM and technical advice regarding its use I would like to thank I-Ning Lee. For synthesis of methallylsilane species I would like to thank Andrew Booth. I would also like to thank my colleagues Emily Sparkes, Morgane Valles and Stephanie Caslin for advice and suggestions and for helping me familiarise myself with the department.
1. Introduction

1.1. Rare Earth Metal Triflates as Water Tolerant Lewis Acid Catalysts

Lewis acids are defined as species with an unfilled valence shell capable of accepting an electron pair from a Lewis base to form a coordinate bond, generating an adduct. Lewis acids such as AlCl₃, ZnCl₂ and TiCl₄ are extensively used as catalysts throughout the petrochemical, bulk chemical and fine chemical industries as they act as particularly effective catalysts in a range of synthetic processes. These include Diels-Alder reactions, Mukaiyama aldol condensations, Friedel-Crafts reactions and other electrophilic aromatic substitutions, and alkene alkylation, dimerisation and polymerisation.

Pressure to reduce the ecological impact of industrial chemical processes has driven research into the adaptation of syntheses traditionally performed in organic solvents to aqueous solvent systems. Water is an attractive solvent due to its non-hazardous nature, low cost, high availability and low environmental impact when disposed of appropriately. However, many classical Lewis acids with high catalytic activity such as the metal halides ZnCl₂, AlCl₃, TiCl₄ and SnCl₄ rapidly undergo displacement reactions with water and decompose to form metal hydroxides or oxides. This renders them ineffective as catalysts for use in aqueous solution. Even trace quantities of water can rapidly deactivate many Lewis acid catalysts.

Though certain water sensitive Lewis acid catalysts such as AlCl₃, TiCl₄ and SnCl₄ can operate in aqueous solvents at low pH ranges the specificity of these conditions limits the applicability of this approach, and catalyst recovery can not be readily performed following the reaction. Efforts have been made to identify water tolerant Lewis acids with high activity under broader physical conditions and that can be recovered with greater ease. Kobayashi et al. have undertaken extensive work to this end and have identified a number of effective Lewis acid catalysts demonstrating high water tolerance.
Kobayashi et al. performed a study in which they screened the water tolerance and catalytic activity of selected group 1 to 15 metal chloride, metal perchlorate and metal trifluoromethanesulfonate (triflate, Tf) Lewis acids in the Mukaiyama aldol reaction of benzaldehyde with (Z)-1-phenyl-1-(trimethylsiloxy)propene (scheme 1)\(^7\).

\[
\text{PhCHO} + \begin{array}{c}
\text{SiMe}_3 \\
\text{O} \\
\text{H}
\end{array} \xrightarrow{\text{MX}_n (0.2 \text{ eq.})} \frac{1 \text{ H}_2\text{O} \cdot 9 \text{ THF}}{\text{RT}, 12 \text{h}} \rightarrow \begin{array}{c}
\text{O} \\
\text{H} \\
\text{C} \\
\text{O} \\
\text{H} \\
\text{Ph}
\end{array}
\]

Scheme 1. The Mukaiyama aldol reaction of (Z)-1-phenyl-1-(trimethylsiloxy)propene with benzaldehyde. MX\(_n = \text{Lewis acid.}

It was observed that species derived from Fe(II), Cu(II), Zn(II), Cd(II), Ln(III) and Pb(II) demonstrated moderate catalytic activity (7-81% yield after 12h dependant on the catalyst and solvent used) while the rare earth metal triflates demonstrated consistently high catalytic activity (78-92% yield after 12h). The remaining metal compounds demonstrated poor or no catalytic activity.

It was noted that the metal cations of the catalytically active Lewis acids share pK\(_h\) values (K\(_h\) = hydrolysis constant) in the range of 4.3 to 10.08 and a water exchange rate constant (WERC) of >3.2\(\times\)10\(^6\) mol\(^{-1}\) s\(^{-1}\), which represents the rate of substitution of water ligands at the metal atom. Table 1 demonstrates these values for selected metal cations and Lewis acids. It can be observed that species with a pK\(_h\) or WERC value outside of the stated range demonstrate poor catalytic activity.
<table>
<thead>
<tr>
<th>Metal Cation</th>
<th>pKₐ</th>
<th>WERC (mol⁻¹.s⁻¹)</th>
<th>Lewis Acid</th>
<th>Product Yield (% w/w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al⁺³</td>
<td>1.1</td>
<td>1.6x10⁰</td>
<td>AlCl₃</td>
<td>trace</td>
</tr>
<tr>
<td>Cr⁺³</td>
<td>4.0</td>
<td>5.8x10⁻⁷</td>
<td>CrCl₃</td>
<td>trace</td>
</tr>
<tr>
<td>Mn⁺²</td>
<td>10.6</td>
<td>3.1x10⁷</td>
<td>MnCl₂</td>
<td>trace</td>
</tr>
<tr>
<td>Co⁺²</td>
<td>9.7</td>
<td>2x10⁵</td>
<td>CoCl₂</td>
<td>trace</td>
</tr>
<tr>
<td>Ni⁺²</td>
<td>9.9</td>
<td>2.7x10⁴</td>
<td>NiCl₂</td>
<td>trace</td>
</tr>
<tr>
<td>Rh⁺³</td>
<td>3.4</td>
<td>3x10⁻⁸</td>
<td>RhCl₃</td>
<td>trace</td>
</tr>
<tr>
<td>In⁺³</td>
<td>4.0</td>
<td>4x10⁴</td>
<td>In(ClO₄)₃</td>
<td>14</td>
</tr>
<tr>
<td>Fe⁺²</td>
<td>9.5</td>
<td>3.2x10⁶</td>
<td>FeCl₂</td>
<td>39</td>
</tr>
<tr>
<td>Cu⁺²</td>
<td>7.5</td>
<td>2x10⁸</td>
<td>Cu(ClO₄)₂</td>
<td>47</td>
</tr>
<tr>
<td>Zn⁺²</td>
<td>9.0</td>
<td>5x10⁸</td>
<td>Zn(ClO₄)₂</td>
<td>46</td>
</tr>
<tr>
<td>Pb⁺²</td>
<td>7.7</td>
<td>7.5x10⁹</td>
<td>Pb(ClO₄)₂</td>
<td>59</td>
</tr>
<tr>
<td>La⁺³</td>
<td>8.5</td>
<td>2.1x10⁸</td>
<td>La(OTf)₃</td>
<td>80</td>
</tr>
<tr>
<td>Ce⁺³</td>
<td>8.3</td>
<td>2.7x10⁸</td>
<td>Ce(OTf)₃</td>
<td>81</td>
</tr>
<tr>
<td>Pr⁺³</td>
<td>8.1</td>
<td>3.1x10⁸</td>
<td>Pr(OTf)₃</td>
<td>83</td>
</tr>
<tr>
<td>Eu⁺³</td>
<td>7.8</td>
<td>6.5x10⁸</td>
<td>Eu(OTf)₃</td>
<td>88</td>
</tr>
<tr>
<td>Dy⁺³</td>
<td>8.0</td>
<td>6.3x10⁷</td>
<td>Dy(OTf)₃</td>
<td>85</td>
</tr>
<tr>
<td>Er⁺³</td>
<td>7.9</td>
<td>1.4x10⁸</td>
<td>Er(OTf)₃</td>
<td>86</td>
</tr>
<tr>
<td>Yb⁺³</td>
<td>7.7</td>
<td>8x10⁷</td>
<td>Yb(OTf)₃</td>
<td>92</td>
</tr>
</tbody>
</table>

Table 1. Comparison of the pKₐ and WERC of various metal cations, and the catalytic activity of derived Lewis acids in the Mukaiyama aldol reaction of benzaldehyde with (Z)-1-phenyl-1-(trimethylsiloxy)propene. Values in red are outside of the ranges proposed to permit effective catalysis (pKₐ 4.3-10.08, WERC >3.2x10⁶ mol⁻¹ s⁻¹).

It was proposed that pKₐ and WERC values within the stated ranges permit rapid ligand exchange. This provides a good rate of coordination of aldehyde molecules with the metal centre, which is required to induce polarisation of the aldehyde to drive its reaction with the enol ether. pKₐ values above 10.08 permit too little coordination of aldehyde molecules with the metal centre while values below 4.3 too easily permit metal hydrolysis, allowing generation of oxonium ions at levels capable of fully decomposing the enol ether thereby inhibiting the reaction. A high WERC permits a high rate of coordination of aldehyde molecules and, by extension, a high rate of catalysis⁷.
In a further study examining the hydroxymethylation of silyl enol ethers using Yb(OTf)$_3$ in tetrahydrofuran (THF) under non-anhydrous conditions (scheme 2) yields of 77-94% were achieved over 24 hours. During workup a liquid-liquid solvent extraction step was used to separate the relatively hydrophobic product from hydrophilic species. Yb(OTf)$_3$ was recovered by precipitation from the aqueous phase of solvent extraction with 91-94% yield$^{9}$. Several other rare earth metal triflates demonstrate similar catalytic activity and stability in aqueous media and have been used in a range of synthetic processes as Lewis acid catalysts$^{10}$.

![Scheme 2. Hydroxymethylation of a generic silyl enol ether in aqueous media by catalysis with Yb(OTf)$_3$.](image)

### 1.2 Scandium Triflate as a Lewis Acid Catalyst in the Silylation of Silanols

The Lewis acid scandium triflate (Sc(OTf)$_3$) has demonstrated effectiveness as a catalyst in a range of classical Lewis acid catalysed reactions including aldol, allylation, Michael, Mannich and Diels-Alder reactions, Friedel-Crafts acylations and Fries rearrangements. The catalyst can generally be recovered during workup by precipitation from the aqueous phase generated during liquid-liquid solvent extraction$^{11}$.

Of particular note is the use of Sc(OTf)$_3$ as a Lewis acid catalyst in the silylation of alcohols with methallylsilanes (scheme 3). This procedure can be performed in aqueous media at room temperature with yields of up to 98% after 30 minutes dependant on the reagents used$^{12}$. 

---

1. Sc(OTf)$_3$: Lewis acid catalyst
2. Scheme 2: Hydroxymethylation of a generic silyl enol ether in aqueous media by catalysis with Yb(OTf)$_3$.
3. 1.2 Scandium Triflate as a Lewis Acid Catalyst in the Silylation of Silanols
4. Sc(OTf)$_3$: Scandium triflate
5. Scheme 3: Silylation of alcohols with methallylsilanes
Scheme 3. General siloxane synthesis by reaction of an alcohol with t-butyldimethyl(2-methallyl)silane.

This procedure inspired a method for grafting methallylsilanes on to oxidised silicon surfaces. Sc(OTf)$_3$ was used to catalyse the silylation of methallylsilanes with a hydroxylated silica surface to generate what was assumed to be a monolayer. The mechanism and structure of bonding was examined by in situ $^1$H nuclear magnetic resonance spectroscopy (NMR) of liberated isobutene during functionalisation, and by $^{13}$C cross-polarisation magic angle spinning NMR (CP-MAS NMR) and elemental analysis of the product gel$^{13}$. The proposed surface structure is shown in scheme 4.

Scheme 4. Functionalisation of an oxidised silicon substrate by Sc(OTf)$_3$ catalysed silylation with a methyl(di(methallyl))silane. R = an unreactive terminal group.

This is significant as predominant contemporary procedures for generation of organic monolayers on silicon substrates require use of independently reactive species such as halosilanes and alkoxysilanes. These compounds are generally applied to the substrate by vapour or liquid phase deposition under carefully controlled conditions$^{14,15}$. Heating may also be required to force grafting. High-quality monolayer generation can be difficult due to reagent
homopolymerisation by hydrolysis in the presence of moisture\textsuperscript{16}. Thus, consistent coating structures are not guaranteed\textsuperscript{17}.

The Sc(OTf)\textsubscript{3} catalysed surface silylation procedure is distinct in its use of methallylsilane reagents which are stable under ambient conditions and in the presence of water. The reaction is effective at room temperature and a range of non-hydroxylated solvents can be used. Unlike alkoxysilanes, methallylsilanes typically do not homopolymerise. As such, and as the reaction of methallylsilanes with the surface is specific, this procedure is likely to generate a relatively consistent monolayer. This principle is illustrated in figure 1. Previous studies have indicated that the Sc(OTf)\textsubscript{3} catalyst may be recoverable in good yield\textsuperscript{11}. Overall this procedure provides a distinct alternative to existing monolayer formation techniques which may facilitate novel approaches to surface functionalisation.

**Figure 1.** Bonding modes of triethoxysilanes and dimethallylsilanes at an oxidised silicon surface. R = an unreactive terminal group. a) Some of the viable bonding modes of ethoxysilanes deposited on oxidised silicon. Further structures are viable due to the many possible homopolymerisation routes of the ethoxysilane. b) The proposed bonding modes of dimethallylsilanes silylated on to oxidised silicon by Sc(OTf)\textsubscript{3} catalysis. When R is an unreactive group and a non-hydroxylated solvent is used, the methallylsilanes can only bond directly to the surface and cannot homopolymerise. Hence, the methallylsilane grafting procedure is more likely to generate monolayers than procedures using ethoxysilanes.
Monolayer formation and other surface modification techniques are performed to attribute surfaces with desirable physical and chemical characteristics. Functionalisation is often performed in stages, using so-called stepwise strategies. For example, the production of surface plasmon resonance biosensors commonly requires the generation of surfaces consisting of biorecognition molecules such as antibodies covalently attached to a metal surface such as gold or silver via a suitable organic linker. This involves several stages of functionalisation, such as the initial deposition of a metal on a suitable substrate such as glass, formation of an organic monolayer coating which is commonly performed by vapour or liquid phase deposition of an alkoxy silane or halosilane to generate a self-assembled monolayer (SAM), and further functionalisation of the SAM to covalently attach the required biorecognition molecule. Secondary functionalisation of the SAM is required when desirable surface functionalities are incompatible with SAM generation, for example due to the presence of moieties which can react with alkoxy silane or halosilane groups via hydrolysis and condensation reactions.

Stepwise strategies are commonly used in lab-on-a-chip, biosensor and organic electronic technologies. The procedure for the Sc(OTf)_3 catalysed grafting of methallylsilanes on to hydroxylated surfaces could potentially be used as an initial grafting process for use in such technologies. Further, it may be possible to reduce the number of functionalisation steps required for certain stepwise fabrication processes if methallylsilanes can be designed to contain appropriate functional groups.

1.3. Scandium Triflate Localisation on Solid Supports

Kobayashi et al. developed a scheme for the localisation of Sc(OTf)_3 on polystyrene supports via an alkylaromatic linker (scheme 5). The polymer-supported catalyst demonstrated high activity in allylation, Diels-Alder and Strecker-type reactions and was easily recovered by filtration. It was reused throughout the study with no observed loss of activity. This procedure could be adapted to permit localisation of Sc(OTf)_3 on other types of support.
Scheme 5. Preparation of a scandium catalyst localised on polystyrene supports via an alkyarylromatic linker.

1.4. Dip Pen Nanolithography

Nanolithography describes a broad range of techniques for the controlled chemical patterning of surfaces with physical features of sub-micron size (typically <100nm). Top-down nanolithography techniques involve the removal or modification of surface material to generate desired features. Bottom-up nanolithography applies material to a surface to generate features.

The development of the atomic force microscope (AFM) permitted nanoscale manipulation of probes and related apparatus, which in turn led to the development of a range of bottom-up nanolithographic procedures. Dip-pen nanolithography (DPN) is perhaps the most well-established of these. Figure 2 depicts a typical DPN procedure. The tip of an AFM probe is coated in a chemical ‘ink,’ typically by submersion in a droplet of pure reagent or a suitable solution. The probe is then brought into contact with a solid substrate and actuated using a piezoelectric motor to deposit the ink on to the surface in precise user-defined patterns via a water meniscus spontaneously generated at the probe apex by condensation of ambient moisture. Features of 50-100nm diameter are typically generated by nanolithographic techniques. The ink can be any molecule physically capable of deposition and can adhere to the
surface by any viable physical interaction such as covalent bonding, hydrogen bonding, ionic bonding and hydrophobic interactions. Covalent bonding is often preferable due to the relative permanence of printed features but this depends on the nature and purpose of surface modification. The chemical ink is selected to provide specific functionality to the lithographed regions. This technology has permitted new advances in nanofabrication, nanoelectronics, biosensors and other technologies.

Figure 2. Stylised depiction of a DPN procedure. a) An AFM probe is coated with a chemical 'ink' by submersion. b) The inked AFM probe is modulated close to a substrate surface. The chemical 'ink' is transferred to the surface via a water meniscus spontaneously generated at the probe apex by condensation of ambient moisture.

1.5. Polymer Pen Lithography

Many nanolithography processes have been developed from the basic DPN concept including catalytic nanolithography, nanofountainprobe lithography and polymer pen lithography (PPL). PPL is a technically interesting case. An elastomeric polymer is applied to a mold or master to produce an array of many equivalent and evenly spaced polymer probes mounted on a support (figure 3a, b). Once mounted on an AFM, the array is precisely aligned with a substrate and is then used to perform multiplexed printing of many identical features over a large area (several cm²) (figure 3c). The development of automated force feedback alignment methods has enhanced the speed and reproducibility of array alignment relative to
manual methods. The master can be designed to determine the form and spacing of the probes and, by extension, those of the printed features. The size of printed features can be varied by altering the contact force of the compressible elastomer probes.

Figure 3. Polymer pen lithography. a) A stylised graphic of a PPL array mounted on a glass support. b) A top-down light microscope image of a PPL array. c) A stylised graphic of parallel printing using dip-pen PPL.

Such parallel printing greatly increases the speed of large area fabrication relative to single probe DPN. In addition, printing over large areas greatly simplifies the challenge of locating printed features during analysis. PPL arrays can be easier to manipulate than single AFM
probes and tend to be more durable. This can be beneficial if probes require treatments such as chemical modifications.

1.6. Catalytic Nanolithography

Catalysts have been employed in nanolithography to induce reaction of reagents with substrate surfaces. This broadens the capabilities of nanolithography as reagents need not have an inherent affinity for the substrate. This permits use of novel reagents and enhances control over adhesion of materials to the surface by providing or denying access to the catalyst\textsuperscript{35}.

Of particular interest are systems in which the catalyst is localised on the lithographic probe. This can be achieved by directly coating the probe with an appropriate metallic catalyst or by binding a catalytic moiety to the probe via a linker. The first reported example of this principle was demonstrated by Müller \textit{et al.}\textsuperscript{41}. A procedure was developed in which a platinum coated AFM probe was used to reduce the terminal azide groups of an alkylazide monolayer on glass substrates submerged in isopropanol that had been saturated with hydrogen gas. The resulting alkylamide patterns were then covalently modified with fluorescin-labelled, aldehyde-modified latex beads to permit imaging of the lithographic features by fluorescence microscopy.

In another example, Mesquita \textit{et al.} reported a procedure in which a manganese complex catalyst tethered to an AFM tip via a decylsilane linker was used to perform localised epoxidation of an alkene monolayer on a silicon substrate\textsuperscript{42}. Figure 4 depicts a stylised illustration of the lithography procedure. Following nanolithography the epoxide sites were reacted with N-octylpiperazine in the presence of catalytic lithium triflate using a non-lithographic chemical treatment. This increased the length of the epoxidised molecules, permitting differentiation between them and non-epoxidised surface molecules by AFM.
**Figure 4.** A schematic illustration of catalytic scanning probe lithography. Representative image of a manganese complex catalyst localised on an AFM probe via a decylsilane linker inducing catalytic epoxidation of grafted silylalkenes with H$_2$O$_2$.

Assuming that the catalytic moiety can not dissociate from the probe, lithographic feature size is essentially defined by the length and flexibility of the chemical linker. Isolating the catalyst to a discreet area of the probe apex may further enhance resolution during lithography. An additional advantage of this approach is that catalytic probes may be reused without reapplication of catalyst. However catalyst cleavage may occur due to exposure of the probe to mechanical forces during lithography.
2. Aims

The aim of this research is to investigate methods for the catalytic nanolithography of methallylsilane species on to oxidised silicon substrates using the Lewis acid catalyst Sc(OTf)$_3$. It has been demonstrated that methallylsilanes react with oxidised silicon substrates in the presence of Sc(OTf)$_3$\textsuperscript{13}. Therefore the focus of this dissertation will be the adaptation of this principle to lithographic techniques. If successful this would permit direct nanoscale functionalisation of oxidised silicon wafer with a variety of methallylsilane-derived species. This is relevant as predominant contemporary techniques for nanolithography of organic compounds on silicon substrates require more extensive pre-functionalisation before lithography, for example by e-beam coating with an appropriate metal or vapour deposition of an alkoxysilane.

Two distinct approaches have been investigated to this end. The first utilises molecular Sc(OTf)$_3$ deposited on oxidised silicon wafer as a catalyst to drive reaction of the hydroxylated surface with a methallylsilane delivered by dip-pen PPL (figure 5).
Figure 5. A representative schematic illustrating catalytic PPL of trimethallylsilanes on to oxidised silicon using a molecular Sc(OTf)$_3$ catalyst deposited on the substrate surface. Only one PPL probe is shown. The trimethallylsilane is physisorbed on to the probe, and is transferred to the surface by the water meniscus. R = an unreactive terminal group.

The second approach investigates means of localising Sc(OTf)$_3$ derived species on PPL arrays composed of a polydimethylsiloxane (PDMS) elastomer to produce a reusable array for catalytic nanolithography. This approach is illustrated in figure 6. A competing reaction may be observed when such arrays are used, as the methallylsilane will be able to react with hydroxy groups at the surface of the PDMS PPL array as well as those on the substrate surface. However, application of a suitably large quantity of the methallylsilane to the array may permit lithography despite the competing reaction, by providing sufficient reagent to permit both reactions to occur and by saturating the hydroxylated sites of the array surface.
Figure 6. A representative schematic illustrating catalytic PPL of trimethallylsilanes on to oxidised silicon using a scandium triflate catalyst bound to a PPL array. Only one PPL probe is shown. The trimethallylsilane is physisorbed on to the probe, and is transferred to the surface by the water meniscus. \( R_1 \) = an organic linker connecting the scandium triflate catalyst to the probe. \( R_2 \) = an unreactive terminal group.
3. Scandium Triflate Catalysed Nanolithography of Methallylsilanes on Oxidised Substrates

3.1. Introduction

This work aimed to develop a procedure for the lithography of methallylsilane species on oxidised silicon substrates. To achieve this, a PPL method for the catalytic lithography of dodecyltris(2-methallyl)silane (DTMS) on an oxidised silicon wafer was employed. Lithographed substrates were compared to substrates generated in control experiments, to give an indication of whether features were produced by the proposed silylation reaction (scheme 6).

![Scheme 6](image)

**Scheme 6.** Sc(OTf)₃ catalysed silylation of an oxidised silicon substrate with dodecyltris(2-methallyl)silane.

PPL permits parallel printing over large cm² areas and this offers the additional advantage of facilitating identification and analysis of surface features. It was also considered that the development of a lithographic procedure using molecular Sc(OTf)₃ may provide insights regarding appropriate conditions for lithography using arrays covalently functionalised with a scandium triflate catalyst, which was a later aim of the project.

3.2 Results and Discussion

Attempts were made to generate lithography features using PPL. Initially Sc(OTf)₃ was applied to oxidised silicon substrates using a dip-coating procedure. Lithography was performed using
PPL arrays inked with DTMS. An extensive range of lithography conditions were used, as detailed in table 2. However, following lithography and washing of the substrates, lateral force AFM (LF-AFM) failed to demonstrate detectable surface features.

<table>
<thead>
<tr>
<th>Procedure</th>
<th>Variable</th>
<th>Units</th>
<th>Minimum</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dip-coating</td>
<td>[Sc(OTf)$_3$]</td>
<td>mmol.l$^{-1}$</td>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td>Lithography</td>
<td>[DTMS]</td>
<td>mmol.l$^{-1}$</td>
<td>5</td>
<td>20</td>
</tr>
<tr>
<td>Humidity</td>
<td>%</td>
<td></td>
<td>15</td>
<td>60</td>
</tr>
<tr>
<td>Temperature</td>
<td>°C</td>
<td></td>
<td>25</td>
<td>35</td>
</tr>
<tr>
<td>Probe Dwell Time</td>
<td>s</td>
<td></td>
<td>1</td>
<td>60</td>
</tr>
<tr>
<td>Development Time</td>
<td>h</td>
<td></td>
<td>1</td>
<td>48</td>
</tr>
</tbody>
</table>

Table 2. Conditions used for polymer pen lithography of DTMS on Sc(OTf)$_3$ dip-coated oxidised silicon substrates. Probe dwell time defines the contact time of the array with the surface in between actuations. Development time describes the time between the completion of lithography and washing the substrate.

It was considered that the dip-coating procedure may be an inappropriate means of applying Sc(OTf)$_3$ to the substrate. A spin-coating procedure for deposition of Sc(OTf)$_3$ was then tested on oxidised silicon substrates. Light microscopy of the spin-coated slides was used to look for visual evidence of inconsistent surface coverage. Microscopy demonstrated a visually even surface with minor occurrence of aberrant features after drying (figure 7).
Figure 7. Optical microscope images of Sc(OTf)$_3$ spin-coated oxidised silicon substrates. a) Surface directly following spin-coating. b) Surface 24 hours after spin-coating.

X-ray photoelectron spectroscopy (XPS) analysis of the spin-coated slides was performed to examine the consistency of distribution of Sc(OTf)$_3$ on the surface. Survey scans were performed at four 300x700µm sites. For each survey scan the Sc 2p signal at 399eV was normalised against the C 1s signal at 281.5eV to provide an approximate indication of the consistency of surface scandium distribution. This carbon signal is primarily generated by adventitious species on the substrate surface. Scandium was detected at each site with levels ranging from 1.36±1.06 relative % atoms to 2.83±0.59 relative % atoms. Illustrative XPS spectra are displayed in figure 8.
Figure 8. XPS spectra of four 300x700µm areas on the surface of an oxidised and Sc(OTf)$_3$ spin-coated silicon wafer. The Sc 2p signal intensity is normalised against the C 1s signal of adventitious surface carbon to provide an indication of the consistency of Sc(OTf)$_3$ distribution. Scandium content relative to surface carbon (relative % atoms): a) 1.36±1.06, b) 2.83±0.59, c) 1.80±0.58, d) 2.15±0.73.

Control substrates composed of oxidised silicon with no further treatment demonstrated no scandium peaks. This suggested that the spin-coated substrates were coated with Sc(OTf)$_3$, though the consistency of its distribution over the whole plate and at areas below 300x700µm were not determined. The inconsistency in values for relative scandium content may be due to experimental inaccuracy resulting from the sensitivity limits of the XPS, or due to actual variations in surface scandium concentrations. XPS scans of higher sensitivity and higher area resolution could be performed to further investigate this.

As XPS analysis indicated that scandium was present on the spin-coated oxidised silicon wafer, PPL was performed on such substrates to examine whether Sc(OTf)$_3$ had been distributed in a
sufficiently consistent manner to permit lithography via the proposed silylation reaction (scheme 6, section 3.1). Following PPL the substrates were washed and imaged by LF-AFM to try and detect and measure the size of lithography features. The PPL conditions used are detailed in table 3. Conditions within the stated ranges permitted production of detectable features except for probe dwell, for which a minimum value of 0.5s was observed to produce features.

<table>
<thead>
<tr>
<th>Variable</th>
<th>Units</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Minimum</td>
</tr>
<tr>
<td>[DTMS] mmol.l⁻¹</td>
<td></td>
<td>20</td>
</tr>
<tr>
<td>Humidity %</td>
<td>%</td>
<td>15</td>
</tr>
<tr>
<td>Temperature °C</td>
<td>°C</td>
<td>25</td>
</tr>
<tr>
<td>Probe Dwell Time s</td>
<td>s</td>
<td>0.25</td>
</tr>
<tr>
<td>Contact Force µN</td>
<td>µN</td>
<td>1</td>
</tr>
<tr>
<td>Development Time h</td>
<td>h</td>
<td>1</td>
</tr>
</tbody>
</table>

Table 3. Conditions used for polymer pen lithography of DTMS on Sc(OTf)₃ spin-coated oxidised silicon substrates. Where only one value is entered no range was used. Probe dwell time defines the contact time of the array with the surface in between actuations. Development time describes the time between the completion of lithography and washing the substrate. Within the stated ranges, development time was not found to have a detectable effect on the size or quality of lithography features. Optimally consistent lithography was demonstrated using 3µN contact force, 30% humidity and dwell time in the range 1-30s. 1s dwell produced features of 2.5±0.39µm mean full width at half maximum (FWHM). FWHM is a measurement of the width of a peak on a graph, and is determined by measuring the distance between the points where the peak is at half of its maximum amplitude relative to a normalised baseline. FWHM values were derived from surface profiles of LF-AFM scans of the lithographed substrates. Figure 9
Figure 9. LF-AFM image of features produced by PPL of DTMS on a Sc(OTf)$_3$ spin-coated oxidised silicon substrate with 30% humidity, 3µN contact force and dwell times of 1s to 30s. a) LF-AFM image of the substrate. b) The lithography template used in the production of lithograph (a) with dwell times. The print area was 50µm$^2$. c) Surface profile of the marked linear region of LF-AFM image (a) with bars indicating the FWHM of the features in this region. d) Table of FWHM values of the features in surface profile (c). The mean FWHM was 2.5±0.28µm.

Optimally sized features were produced using 15% humidity during lithography, 500ms dwell time and 1µN contact force. Under these conditions a mean feature size of 439±70nm was achieved. It is assumed that the reduced contact force caused a lesser area of the PDMS
probes to contact the surface. This would reduce the area of the probe sufficiently close to the surface to permit transferal of DTMS via the water meniscus, which would cause the DTMS to be transferred to a smaller area of the substrate during each contact event. The reduced dwell time may have provided less time for transeral of DTMS to the surface, which may have further limited its dispersion over the surface. The reduced humidity may also have influenced the feature diameter as the water meniscus responsible for transferal of material may have been smaller, reducing the rate of DTMS transfer and limiting the area it could transfer to. Figure 10 shows LF-AFM images of a substrate printed under the above conditions.

**Figure 10.** LF-AFM images of features produced by PPL of DTMS on a Sc(OTf)$_3$ spin-coated oxidised silicon substrate with 15% humidity, 1µN contact force and dwell times of 750ms to 100ms. a) 50µm$^2$ LF- AFM image of an oxidised silicon substrate with features produced by PPL using DTMS in the presence of Sc(OTf)$_3$. b) A higher resolution scan of the marked square region of LF-AFM image (a) with 12.5µm$^2$ area and 49nm pixel size. c) The lithography template used in production of lithograph (a) with dwell times. The print area was 50µm$^2$. Comparison of this image to (a) demonstrates that features are not present at all intended locations.
It can be observed that features are not present at all intended coordinates when lower dwell times are used. This could partially be due to suboptimal distribution of Sc(OTf)$_3$ on the substrate surface. Some locations may contain insufficient catalyst to induce DTMS silylation. The effects of this may be particularly pronounced under the lithography conditions used when printing smaller features. Lithography at high humidity and contact force would be expected to generate relatively large water menisci at the apex of the PDMS probes, which would contact a relatively large area of the substrate. Sc(OTf)$_3$ within that area may be redistributed by the meniscus, permitting effective catalysis over the contacted area of the substrate. However lithography using a low contact force or low humidity would be expected to generate a smaller meniscus. If small areas of low Sc(OTf)$_3$ concentration are present on the surface, it would become more probable that the area of the substrate contacted by the meniscus could contain too little Sc(OTf)$_3$ for effective catalysis, even when redistribution of Sc(OTf)$_3$ by the meniscus is accounted for.

Alternatively the transferal of DTMS to the surface may be inconsistent, as the reduced humidity and contact force used may have resulted in unreliable meniscus generation. Further refinement of the conditions of lithography may therefore permit the printing of small features with improved consistency.

Two control lithography tests were performed under the conditions stated in table 4. Previously these conditions demonstrated features of 3.27±0.38µm FWHM when Sc(OTf)$_3$ and DTMS were present. However, in these control experiments, when either DTMS or Sc(OTf)$_3$ was omitted no features could be detected by LF-AFM. This suggests that the observed features were produced by catalytic silylation of DTMS with the oxidised silicon substrate.
### Table 4. Control lithography experiments. Under standard lithography conditions using Sc(OTf)₃ and DTMS features of 2.5±0.28µm FWHM were detected by LF-AFM. In the absence of either Sc(OTf)₃ or DTMS no lithographic features could be detected by LF-AFM. *Pure ethanol was used in place of reagents in the control experiments.

<table>
<thead>
<tr>
<th>Procedure</th>
<th>Variable</th>
<th>Units</th>
<th>Standard Conditions</th>
<th>Control Conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spin-coating</td>
<td>[Sc(OTf)₃]</td>
<td>mmol.l⁻¹</td>
<td>20</td>
<td>20 0*</td>
</tr>
<tr>
<td>Lithography</td>
<td>[DTMS]</td>
<td>mmol.l⁻¹</td>
<td>20</td>
<td>0* 20</td>
</tr>
<tr>
<td>Humidity</td>
<td>%</td>
<td></td>
<td>30</td>
<td>30 30</td>
</tr>
<tr>
<td>Temperature</td>
<td>°C</td>
<td></td>
<td>25</td>
<td>25 25</td>
</tr>
<tr>
<td>Probe Dwell</td>
<td>s</td>
<td></td>
<td>1</td>
<td>1 1</td>
</tr>
<tr>
<td>Contact Force</td>
<td>µN</td>
<td></td>
<td>3</td>
<td>3 3</td>
</tr>
<tr>
<td>Development Time</td>
<td>h</td>
<td></td>
<td>1</td>
<td>1 1</td>
</tr>
</tbody>
</table>

### 3.3. Conclusion

This section of the project fulfils the aim of developing a procedure for the lithography of a methallylsilane on oxidised silicon substrates by Sc(OTf)₃ catalysed PPL. Lithographic features of 2.5±0.28µm FWHM diameter were produced with good reliability and repeatability. Smaller features of 439±70nm FWHM diameter were successfully generated but with limited reliability, as some features were absent from the intended lithographic pattern.

The limited reliability of the procedure used to print the smaller features suggests that conditions need to be adjusted to facilitate more consistent transferal of reagents to the surface while maintaining a small print size. Increasing the humidity during lithography may achieve this. Larger features were observed at higher humidities but appropriate modulation of contact force
and dwell time may permit counteractive feature size reduction. Alternatively it may be that the Sc(OTf)₃ spin-coating procedure does not distribute the catalyst over the substrate surface in a sufficiently even manner. Adjustment of the spin coating procedure may address this.

Control experiments indicated that the detected lithography features were produced by Sc(OTf)₃ catalysed silylation of methallylsilanes with silanol groups at the oxidised silicon surface. However further analysis should be performed to verify that the features are covalently bound methallylsilane derivatives. The DTMS used in this study is a non-ideal candidate for further analysis due to its chemical composition. The alkylsilane coating generated by the silylation reaction may be difficult to differentiate from adventitious carbon at the substrate surface, and from the silicon substrate itself. Analytical processes poorly suited to differentiation of this molecule from adventitious species under the current lithography conditions include XPS, elemental analysis and Raman spectroscopy.

A methallylsilane could be designed that contains or permits attachment of a fluorescent moiety. This could be used in PPL to facilitate analysis. Lithography using such a compound followed by fluorescence microscope imaging would permit confirmation of the lithographed species’ origin, though the bonding mechanism would not be incontrovertibly evidenced. Examples of this approach exist in published literature⁴³.

XPS would not permit detection of grafted DTMS on oxidised silicon due to convolution of its carbon signal with that produced by adventitious surface carbon but it may be capable of detecting a novel methallylsilane of sufficiently distinct elemental composition. For example a methallylsilane containing fluorine could be used. Features produced using this species would be expected to demonstrate a distinct binding energy at ~689eV. Alternatively an amine moiety would be expected to demonstrate a distinct binding energy at ~400eV. These signals may be
distinguishable from the substrate and adventitious surface species. However this approach would not evidence the mode of bonding of the grafted species to the substrate.

Secondary ion mass spectrometry (SIMS) may be a suitable procedure for determining the empirical structure of surface groups and evidence of the mode of bonding to the substrate by identification of molecular ions with mass equivalent to that of the proposed surface species plus numerous silicon atoms. Differentiation of such signals from adventitious surface compounds may be challenging but comparison to references and use of methallylsilanes containing elements with distinct mass may make this a viable approach\textsuperscript{44,45}. 
4. Fabrication of Scandium Triflate Functionalised PPL Arrays

4.1. Introduction

The aim of this body of work was the production of materials functionalised with localised scandium triflate (R-Sc(OTf)$_2$) to allow development of functionalised PPL arrays suitable for catalytic nanolithography of methallylsilanes on oxidised silicon substrates. It was initially proposed that an existing approach to R-Sc(OTf)$_2$ functionalisation of polystyrene beads would be employed\textsuperscript{26}. This was to be tested on oxidised silicon substrates to permit analysis prior to extension of the method to PDMS PPL arrays.

4.2. Results and Discussion

4.2.1. Functionalisation of Oxidised Silicon Wafer with Scandium Triflate

Two methods for the functionalisation of oxidised silicon surfaces with R-Sc(OTf)$_2$ were proposed. For both methods, the synthetic scheme began with functionalisation of the substrate surface with an alkylsulfonic acid moiety. Vapour deposition of 3-mercaptopropyltrimethoxysilane (3-MPTMS) was performed on oxidised silicon wafer\textsuperscript{46} to generate substrate A (scheme 7). Substrate A was then exposed to a solution of potassium peroxymonosulfate (Oxone\textsuperscript{6}) for 36 hours to oxidise the thiol to sulfonic acid\textsuperscript{47} to generate substrate B (scheme 7).
Scheme 7. Functionalisation of an oxidised silicon substrate surface with an alkylsulfonic acid moiety.

At this point the functionalisation procedures diverged. To generate the R-Sc(OTf)$_2$ functionalised substrate D (scheme 8), substrate B was first treated with scandium(III) chloride (ScCl$_3$) to induce exchange of the thiol's proton with scandium chloride, to generate substrate C (scheme 8). Substrate C was then exposed to an aqueous solution of trifluoromethanesulfonic acid to substitute the chloride atoms of the scandium salt with triflate groups. These two functionalisation steps were adapted from literature.$^{26}$

Scheme 8. Conversion of a sulfonic acid functionalised substrate to a scandium triflate functionalised substrate by reaction with ScCl$_3$ followed by TfOH.
A second process avoiding use of TfOH was developed, in part due to the highly hazardous nature of the compound and its potential to damage the substrate but also to see if a simplified process was viable. Substrate B was directly treated with aqueous Sc(OTf)$_3$ to try and induce coordination of the sulfonic acid with Sc(OTf)$_3$, potentially generating R-Sc(OTf)$_2$ functionalised substrate E (scheme 9).

Scheme 9. Conversion of a sulfonic acid functionalised substrate to a scandium triflate functionalised substrate by direct reaction with Sc(OTf)$_3$.

4.2.2 Surface Analysis of the Functionalised Substrates.

Water contact angle goniometry (CAG) was performed on substrates A to E, to provide an initial indication of whether functionalisation had taken place. The results are shown in table 5.
<table>
<thead>
<tr>
<th>Substrate</th>
<th>Proposed Structure</th>
<th>H₂O Contact Angle (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxidised Silicon</td>
<td><img src="image" alt="Structure" /></td>
<td>33.2±0.4</td>
</tr>
<tr>
<td>A</td>
<td><img src="image" alt="Structure" /></td>
<td>55.2±0.3</td>
</tr>
<tr>
<td>B</td>
<td><img src="image" alt="Structure" /></td>
<td>17.9±0.3</td>
</tr>
<tr>
<td>C</td>
<td><img src="image" alt="Structure" /></td>
<td>34.7±0.8</td>
</tr>
<tr>
<td>D</td>
<td><img src="image" alt="Structure" /></td>
<td>46.5±0.3</td>
</tr>
<tr>
<td>E</td>
<td><img src="image" alt="Structure" /></td>
<td>26.0±0.3</td>
</tr>
</tbody>
</table>

*Table 5. Water contact angles of functionalised silicon substrates determined by water contact angle goniometry. Stated contact angles are mean values produced from three readings at different sites on the substrate similar to ±2°.*

The contact angle of the thiol functionalised substrate A produced by vapour deposition of 3-MPTMS (55.2±0.3°) approached experimental values from literature for comparable surfaces produced by vapour deposition of 3-mercaptopropyltriethoxysilane on oxidised silicon (40.3±0.3°)⁴⁸, though discrepancy is clear. This may be attributed to variation in the reagent, surface
preparation and vapour deposition methods used. Nonetheless the increase in contact angle is consistent with the expected increase in hydrophobicity of the surface upon alkylation.

Experimental values for the remaining substrates could not be found. However trends in contact angle variation can be compared. With the exception of substrate D the trend in contact angle corresponded to what would be expected given the relative hydrophilicities of the intended surface functionalities. The oxidised silicon substrate, sulfonic acid substrate B and R-Sc(OTf)$_2$ substrate E demonstrated relatively high hydrophilicity while the remaining substrates demonstrated relative hydrophobicity. Further, an observable increase in contact angle occurred between substrates B and E, indicating that a change occurred on exposure to Sc(OTf)$_3$ which resulted in increased surface hydrophobicity. The cause of the unexpected hydrophobicity of substrate D and substantial chemical information regarding the surfaces are not provided by this analytical procedure.

In order to further investigate these observations XPS analysis was performed on the functionalised substrates. This data was used to determine the relative atomic concentrations of scandium, fluorine, carbon and carbon local to electron withdrawing groups (EWGs) on the substrate surface. These values for species of interest are shown in table 6. Two distinct carbon concentrations were determined because carbon atoms local to EWGs experience chemical shift during XPS analysis and can produce an XPS signal distinct from that of other carbon species. Sulfonic acid and sulfonyl groups act as EWGs, and so this distinct signal can be used to evidence their presence. XPS was also performed on oxidised and un-oxidised silicon wafer, which acted as control substrates.
<table>
<thead>
<tr>
<th>Substrate</th>
<th>Proposed Structure</th>
<th>Relative % Atoms</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Sc (402.5eV)</td>
<td>C (EWG-local)</td>
<td>F (685eV)</td>
</tr>
<tr>
<td>Silicon Wafer</td>
<td>Si</td>
<td>0.00±0.00</td>
<td>0.00±0.00</td>
<td>0.00±0.00</td>
<td></td>
</tr>
<tr>
<td>Oxidised Silicon Wafer</td>
<td>Si-OH</td>
<td>0.00±0.00</td>
<td>0.00±0.00</td>
<td>0.00±0.00</td>
<td></td>
</tr>
<tr>
<td>A</td>
<td>S-OH</td>
<td>0.00±0.00</td>
<td>0.00±0.00</td>
<td>7.40±0.47</td>
<td></td>
</tr>
<tr>
<td>B</td>
<td>S-OH</td>
<td>0.00±0.00</td>
<td>2.47±0.62</td>
<td>0.85±0.40</td>
<td></td>
</tr>
<tr>
<td>C</td>
<td>S-OH</td>
<td>12.77±0.56</td>
<td>5.51±0.49</td>
<td>1.23±0.35</td>
<td></td>
</tr>
<tr>
<td>D</td>
<td>S-OH</td>
<td>0.00±0.00</td>
<td>0.00±0.00</td>
<td>1.28±0.41</td>
<td></td>
</tr>
<tr>
<td>E</td>
<td>S-OH</td>
<td>3.59±0.34</td>
<td>3.36±0.39</td>
<td>2.40±0.21</td>
<td></td>
</tr>
</tbody>
</table>

**Table 6.** XPS analysis of oxidised and un-oxidised silicon wafer, and substrates A to E. The relative percentage of atoms of scandium, fluorine, EWG-local C and non-EWG-local C were calculated. Values for the former three species are shown. Each value is the mean of 3 measurements produced using data extracted from 3 different 400x800µm regions of a substrate.
Certain elements of interest can not be analysed in this instance. Signals produced by atomic sulfur convolute with strong silicon signals produced by the substrate, preventing differentiation of the two. Carbon not local to an EWG can not be differentiated from adventitious surface carbon which naturally develops in high relative concentrations at the substrate surface by atmospheric exposure.

However, the C 1s signal produced by carbon local to an EWG can be scrutinised. This signal is only present in the spectra for substrates B, C and E, which may indicate the presence of the intended sulfonic acid and sulfonyl moieties on these substrates. Signals for scandium can be clearly observed in substrates C and E, evidencing its presence.

It was originally considered that analysis of the fluorine signals of the XPS spectra could be used to identify triflate groups in order to provide evidence of R-Sc(OTf)$_3$ functionalisation. However, fluorine signals are seen in all of the spectra of substrates A to E. This is surprising as only substrates D and E were intentionally exposed to compounds containing fluorine during fabrication. Fluorine is not observed in the control spectra produced by XPS of oxidised and unoxidised silicon wafers.

It could be that substrate A was contaminated during fabrication, leading to fluorine being present on the substrates produced thereafter, though no obvious source of fluorine exists within the fabrication procedure employed. Alternatively contamination could have taken place after substrate fabrication. The control substrates were analysed at the University of Manchester, whereas substrates A to E were analysed by the NEXUS XPS service at the University of Newcastle. As such a variation in sample handling or XPS analysis procedure could explain why fluorine is observed on the functionalised substrates but not on the control substrates. However, potential sources of contamination are not evident. Illustrative spectra demonstrating the signals produced by elements of interest are shown in figure 11.
Substrate D demonstrates no scandium or EWG-local carbon. This suggests that exposure to triflic acid may have removed species from the surface. This goes some way toward explaining its hydrophobicity demonstrated during water CAG analysis. It can be assumed that the adopted approach to R-Sc(OTf)$_2$ functionalisation using TfOH is not suitable for this functionalisation procedure. Illustrative XPS spectra of substrate D are shown in figure 12.
Figure 12. XPS spectra of substrate D. a) An XPS survey spectrum of substrate D. It can be observed that no signal is present for scandium (Sc 2p signal, 402eV). This suggests that scandium is not present on the substrate surface at a concentration detectable using this XPS procedure. b) The C 1s region of the XPS spectrum of substrate D. The large C1s signal at 284.6eV representative of adventitious carbon is present. However the smaller C1s signal at 288.2eV representative of carbon local to an electron withdrawing group is absent. As the precursor substrate C demonstrated this shifted C 1s signal, this suggests that surface functionality was lost during the treatment of substrate C with TfOH.

A limitation of this analytical method is its inability to determine the structure and surface bonding mode of the detected species. They may not be covalently attached to the substrate. Approaches to determining this are discussed in the Conclusion section.

4.2.3. Further Attempts at Structural Analysis of the Functionalised Substrates

Fourier transform infrared spectroscopy (FTIR) was performed on the functionalised substrates. The spectra produced by functionalised substrates were indistinguishable from those produced by oxidised silicon wafer, presumably due to the low concentration of surface species.

Extensive attempts to generate additional data by Raman spectroscopy were made using depth profiling techniques. If successful this approach may have permitted identification of various
functionalities including thiol, sulfonic acid and triflate groups. However relevant features could not be discerned from the strong background signal generated by the oxidised silicon surface. 

Attenuated total reflection infrared spectroscopy (ATR-IR) was considered as a means of identifying surface functionalities. Preliminary analyses of the substrates failed to demonstrate evidence of surface groups and indicated that substantial time would need to be devoted to development of a suitable analytical procedure. Due to the time restraints of the project and uncertainty regarding whether the procedure would permit surface species detection this approach was not adopted.

4.2.4. Catalytic Activity Test of Functionalised Substrate E

Due to the limited amount of spectroscopic data indicating the presence of the intended $\text{R-Sc(OTf)}_2$ functionality on the functionalised substrate surfaces, attempts were instead made to test the catalytic activity of the proposed substrates. A preliminary catalytic activity test was developed based on the $\text{Sc(OTf)}_3$ catalysed silylation of triisopropylsilanol (TIPS) with (methallyl)trimethylsilane (MATS) to generate $1,1,1$-triisopropyl-$3,3,3$-trimethyldisiloxane (TTDS). A known concentration of tetraethylsilanol (TES) was also included in the reaction mixture, to act as an internal standard. In place of $\text{Sc(OTf)}_3$, eight $4\text{cm}^2$ pieces of substrate E were placed in the reaction vessel to assess their catalytic activity (scheme 10). A comparative reaction was performed using molecular $\text{Sc(OTf)}_3$ catalyst (2mol%) in place of substrate E, and a control reaction was performed with no catalyst or substrate present. Samples were taken periodically and analysed by GCMS. Results are shown in figure 13.
Scheme 10. Proposed scheme for the catalytic activity test of substrate E.

Figure 13. Catalytic activity test results. Reagent abundances were normalised against an internal standard of TES (5mmol.l⁻¹). a) Catalytic activity test using eight 4cm² plates of substrate E as a catalyst. b) Comparative reaction using molecular Sc(OTf)₃ as a catalyst. c) Control reaction performed without a catalyst.
The comparative catalytic activity test in which Sc(OTf)$_3$ was used as a catalyst demonstrated product generation and depletion of reagents TIPS and MATS. However the catalytic activity test using substrate E demonstrated no product generation. Nor did the control test in which no catalyst or substrate was used. This indicates that substrate E may not possess catalytically active R-Sc(OTf)$_2$. Alternatively it may indicate that the concentration of R-Sc(OTf)$_2$ is too low to permit substantial catalysis over the timeframe of the test.

Surprisingly, isolated depletion of MATS was observed in the test in which substrate E was used, and in the control reaction. These tests were repeated and in each instance this phenomenon was observed. The boiling point of MATS is 109°C and the tests were performed using vessels tightly covered with parafilm so loss by evaporation is unlikely. This may evidence a competing reaction, though no additional product could be identified by GCMS.

Quantitative analysis using GCMS standards and analysis of the catalytic product were not performed as a lack of positive results rendered this unnecessary. Time limitations prevented further consideration of the catalytic activity test.

4.2.5. Lithography using Functionalised PPL Arrays

As XPS analysis indicated that scandium was present on substrate E the functionalisation process used to create it was performed on PDMS PPL arrays. These were employed in attempts to perform catalytic nanolithography of DTMS on oxidised silicon.

Following the functionalisation process the arrays were scrutinised by light microscope to assess their condition. No observable damage was present. PPL of DTMS on oxidised silicon was attempted at 15% to 60% humidity in 15% increments with a contact force of 3μN and dwell times from 1 to 30 seconds. Visible features were not generated by this procedure.
4.3. Conclusion

Two R-Sc(OTf)$_2$ functionalisation procedures were proposed and executed on oxidised silicon wafer. Water CAG and XPS analyses demonstrated a degree of surface modification. The latter procedure identified scandium on one of the proposed r-Sc(OTf)$_2$ functionalised substrates, but not the other. Attempts to perform more extensive substrate analysis were unsuccessful, as were initial catalytic activity tests. The procedure has not been successfully applied to a protocol for catalytic PPL of methallylsilanes on oxidised silicon substrates.

It is clear that further work is required to achieve the aims of this section of the project. The functionalised substrate analyses performed to date provide some information regarding the nature of the modified substrates but it is inconclusive regarding the chemical structure and bonding mode of surface species. Further analysis is required to this end.

Performing the functionalisation procedures on gold coated substrates may enhance signals generated by Raman spectroscopy through surface-enhanced Raman scattering, permitting structural analysis of the surface species. This approach is expected to be incompatible with the procedure utilising TfOH, which would dissolve the metal coating.

Applying the functionalisation procedures to silica gel or a similar high surface area substrate would permit generation of far higher concentrations of surface functionalities. Such gels could be analysed by $^{13}$C CP-MAS NMR to permit more extensive scrutiny of the structure of the surface species.

SIMS may allow determination of surface group structure and bonding mode by analysis of mass fragmentation patterns, as was discussed in section 3.3.
Following appropriate analysis, if the intended functionality is shown to be present on the functionalised substrates then the functionalisation procedure could be optimised to try and increase grafted $\text{R-Sc(OTf)}_2$ concentrations. The procedure could then be extended to PDMS, and PPL could be attempted under broader conditions.
5. Conclusions

Nanolithography was performed by PPL of DTMS on oxidised silicon substrates spin-coated with Sc(OTf)$_3$. A minimum feature size of 439±70nm was achieved with moderate reliability. Absence of features at some positions on the functionalised substrate indicate that further adjustments are required for reliable lithography of features at this scale, such as adjustment of the humidity and dwell time parameters, increasing the concentration of the DTMS solution and re-examination of the Sc(OTf)$_3$ spin-coating procedure. Larger features of 2.5±0.28µm were produced with good reliability and repeatability.

Reference studies indicated that the proposed silylation reaction (scheme 6, section 3.1.) produced the surface features but further analysis should be performed to verify this. XPS of features produced by PPL using a methallylsilane species containing nitrogen or fluorine, lithography using a fluorescent methallylsilane, and SIMS could be employed to this end. These approaches to analysis are discussed in further detail in section 3.3. If the structure of the lithographed species is demonstrated to be as predicted this procedure may then be attempted using other methallylsilanes, to demonstrate its application in the direct patterning of various organic species on oxidised silicon. Coupled with further refinement of the lithography procedure to generate smaller features this could provide a considerably simplified method for the generation of nanopatterned silicon substrates suitable for use in nanofabrication technologies.

Production of catalytic PPL arrays functionalised with localised R-Sc(OTf)$_2$ was not demonstrably achieved. Two functionalisation schemes were developed and performed on oxidised silicon substrates. It was demonstrated by water CAG that some form of surface modification had taken place. Trends in contact angles approximately corresponded with those expected given the relative hydrophilicities of the intended functionalities with the exception of substrate D (scheme 8, section 4.2.1.). XPS demonstrated the presence of scandium, and
provided evidence of EWG-local carbon which may be proximal to sulfonic acid or sulfonyl moieties, on the appropriate substrates. The exception to this is substrate D which appears to have undergone surface cleavage, possibly due to its exposure to TfOH during fabrication. Use of a milder TfOH solution may permit functionalisation with reduced cleavage. The conditions used to neutralise the TfOH after surface treatment (section 6.4.5.) should also be scrutinised to determine whether this may have affected the substrate surface.

The structure, full chemical composition and bonding mode of the surface species were not determined. This will be required for reasoned assessment of the functionalisation protocol. Application of the functionalisation procedures to gold coated substrates may enhance Raman spectroscopy signals by surface enhanced Raman scattering, permitting further characterisation. $^{13}$C CP-MAS NMR of silica gel functionalised in the same manner as the substrates is a promising approach to scrutiny of the structure of the organic surface species$^{13,50}$. SIMS may also permit surface group structure and bonding mode determination. These approaches to analysis are discussed in greater detail in section 4.3.
6. Experimental

6.1. Materials

6.1.1. General Materials

Chemicals were purchased from Sigma-Aldrich unless otherwise stated. Solvents were of HPLC or analytical grade. Ultrapure water prepared by Milli-Q filtration (Merck Millipore) was used unless otherwise stated. Silicon substrates were silicon (100) wafer. Sc(OTf)$_3$ was purchased from Fluorochem Limited (Fluorochem, Derbyshire, UK). Dodecyltris(2-methallyl)silane was synthesised by Andrew Booth according to previously reported procedures$^{12}$.

6.1.2. PPL and AFM

ContAl-G AFM cantilevers were used for LF-AFM imaging (Budget Sensors, Bulgaria). Silicon masters for PPL array production were purchased from NIL Technology ApS (Kongens Lyngbg, Denmark). A schematic of the array dimensions is shown in figure 14.

![Figure 14. PPL master dimensions. This pattern was repeated across the surface of one face of the master. Total array size: 20mm$^2$.](image)
6.1.3. Fabrication of PPL Arrays

Protocol for producing PDMS PPL arrays was based on literature\textsuperscript{37} and adapted by Joseph Hosford. A 1-2cm\textsuperscript{2} glass microscope slide piece was sonicated in ethanol (10min) and oxidised by oxygen plasma treatment. A PPL master was sonicated in ethanol (10min). (7-8\% w/w vinyldimethylsiloxane)-dimethylsiloxane co-polymer (VDT-931, Fluorochem, 250g), platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane (SIP6831.1, Gelest, 10µl) and 2,4,6,8-tetramethyl-2,4,6,8-tetravinylcyclotetrasiloxane (172µl) were combined and mixed for 7 days. 1.7g of this mixture was combined with (25-35\% w/w methylhydrosiloxane)-dimethylsiloxane (HMS-301, Fluorochem, 0.5g) and degassed under vacuum. ~100µl of this elastomer mixture was applied to the engraved face of the master using a pipette. The elastomer-coated master was then degassed under vacuum. The oxidised face of the glass piece was applied to the elastomer mixture on the coated master with mild pressure. This construct was heated in an autoclave at 90°C for 16h to cure the PDMS. The glass piece with adhered PDMS PPL array was extracted from the master. A border of 1-2mm was trimmed from the edges of the PDMS PPL array using a razor blade. Masters were soaked in toluene (16h) and sonicated in toluene (15min) after use.

6.2. Equipment

6.2.1. General Equipment

Substrate and array oxidation by plasma cleaning was performed using a Plasma Cleaner PDC-32G-2 with Plasmaflo PDC-FMG-2 (Harrick Plasma, New York, USA). Spin-coating was performed using a Laurell WS-650MZ-23NPP (Laurell Technologies Corporation, Pennsylvania, USA). CAG was performed using a Theta Lite Optical Tensiometer TL101 (Biolin Scientific, Espoo, Finland).
6.2.2. AFM and PPL

A Nanosurf FlexAFM with C3000 controller (Nanosurf AG, Liestal, Switzerland) was used for lithography and imaging. This was mounted above a motorised translation and goniometer stage with integrated pressure sensors, which was custom-built by Nanosurf. The pressure sensors permitted measurement of the pressure of PPL array contact with substrates. A custom holder was used to mount PPL arrays on the AFM. Humidity was controlled using a ProUmid Modular Humidity Generator (ProUmid, Ulm, Germany). Low humidity was achieved using an 
N₂ gas line.

6.3. Analysis

6.3.1. XPS

XPS of functionalised substrates A to E (section 4.2.1) was performed by staff at the EPSRC NEXUS facility at the University of Newcastle using a K-Alpha (Thermo Scientific, East Grinstead, UK) according to the parameters below (table 7).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-ray source</td>
<td>Microfocused monochromatic AlKa</td>
</tr>
<tr>
<td>X-ray energy</td>
<td>1486.6eV</td>
</tr>
<tr>
<td>X-ray current</td>
<td>12kV</td>
</tr>
<tr>
<td>X-ray voltage</td>
<td>3mA</td>
</tr>
<tr>
<td>Spot size</td>
<td>400x800µm</td>
</tr>
<tr>
<td>Emission angle</td>
<td>0°</td>
</tr>
<tr>
<td>Pass energy</td>
<td>150eV</td>
</tr>
<tr>
<td>Step size</td>
<td>0.4eV</td>
</tr>
<tr>
<td>Charge neutralisation used</td>
<td>Yes</td>
</tr>
<tr>
<td>Vacuum pressure</td>
<td>&lt;3x10⁻⁸ mbar</td>
</tr>
</tbody>
</table>

Table 7. XPS parameters (K-Alpha, NEXUS, University of Newcastle).
XPS of all other substrates was overseen by Dr. Ben Spencer at the XPS facility at the School of Materials, University of Manchester, and performed using an Axis Ultra Hybrid (Kratos Analytical, Manchester, UK) according to the parameters below (table 8).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>X-ray source</td>
<td>Microfocused monochromatic AlKa</td>
</tr>
<tr>
<td>X-ray energy</td>
<td>1486.7eV</td>
</tr>
<tr>
<td>X-ray current</td>
<td>15kV</td>
</tr>
<tr>
<td>X-ray voltage</td>
<td>10mA</td>
</tr>
<tr>
<td>Spot size</td>
<td>300x700µm</td>
</tr>
<tr>
<td>Emission angle</td>
<td>0°</td>
</tr>
<tr>
<td>Pass energy</td>
<td>80eV</td>
</tr>
<tr>
<td>Step size</td>
<td>0.5eV</td>
</tr>
<tr>
<td>Charge neutralisation</td>
<td>Yes</td>
</tr>
<tr>
<td>Vacuum pressure</td>
<td>&lt;3x10^-8 mbar</td>
</tr>
</tbody>
</table>

*Table 8. XPS parameters (Axis Ultra Hybrid, University of Manchester).*

6.3.2. AFM

AFM imaging was performed in lateral force mode with 256 points per line and 15nN setpoint. A nominal value of 0.2N/m was used for the cantilever stiffness based on the manufacturer’s specifications.

6.3.3. CAG

Water CAG was performed using deionised water. Three locations were analysed on each substrate.
6.3.4. GCMS

GCMS was performed using a Finnigan Trace GC Ultra with Finnigan Polaris Q ion source from Thermo Electron (Thermo Fischer Scientific, Massachusetts, USA) according to the parameters in Table 9.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carrier gas</td>
<td>99.9995% ultra high purity helium</td>
</tr>
<tr>
<td>GC inlet temperature</td>
<td>200°C</td>
</tr>
<tr>
<td>Injection Volume</td>
<td>1uL</td>
</tr>
<tr>
<td>Split Flow</td>
<td>10min.ml⁻¹</td>
</tr>
<tr>
<td>Transfer line temperature</td>
<td>275°C</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Temperature program</th>
<th>Ramp (°C.min⁻¹)</th>
<th>Temperature (°C)</th>
<th>Hold (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>60</td>
<td>2</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>250</td>
<td>6</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>300</td>
<td>2</td>
<td></td>
</tr>
</tbody>
</table>

Table 9. GCMS conditions.

6.3.5. Catalytic Activity Test of Substrate E

For the catalytic activity test of substrate E, triisopropylsilanol (435mg, 2.5mmol), (methallyl)trimethylsilane (320mg, 2.5mmol) and tetraethylsilane (360.75mg, 2.5mmol) were dissolved in THF (500ml) in a large beaker. A small glass petri dish containing a magnetic stirring bar was placed in the solution at the centre of the beaker. Eight 4cm² samples of substrate E were added to the solution at the periphery of the beaker with their functionalised faces pointing upwards. This setup is illustrated in figure 15. The petri dish was included to prevent the magnetic stirring rod from contacting and damaging the substrates. Caution was taken to ensure that the functionalised face of the substrates did not contact any surfaces. The solution was gently stirred using the magnetic stirrer for 48 hours. 2ml samples of the reaction solution were periodically extracted and analysed by GCMS.
Figure 15. Apparatus setup for the catalytic activity test of substrate E. The petri dish is included to prevent contact of the magnetic stirring rod with the substrates.

For the comparative reaction using $\text{Sc(OTf)}_3$ and the control in which no catalyst was used, triisopropylsilanol (174mg, 1mmol), (methallyl)trimethylsilane (128mg, 1mmol) and tetraethylsilane (144.3mg, 1mmol) were dissolved in THF (200ml). Either $\text{Sc(OTf)}_3$ (9.84mg, 0.02mmol) or no catalyst was added to the solution. The solution was gently stirred using a magnetic stirrer for 48 hours. 2ml samples of the reaction solution were periodically extracted and analysed by GCMS.

6.4. Molecular $\text{Sc(OTf)}_3$ Nanolithography Methods

6.4.1. General Procedures

Silicon substrates were oxidised by oxygen plasma cleaning for 3 minutes at high setting. $\text{Sc(OTf)}_3$ dip-coated oxidised silicon substrates were produced by submerging oxidised Si wafer in $\text{Sc(OTf)}_3$ (5mM solution: 73.5mg, 0.15mmol; 20mM solution: 294mg, 0.6mmol) in water (30ml) for 16h followed by drying with a gentle stream of $\text{N}_2$. $\text{Sc(OTf)}_3$ spin-coated oxidised silicon substrates were produced by spin-coating oxidised silicon substrates with 25µl of $\text{Sc(OTf)}_3$ (294mg, 0.6mmol) in ethanol (30ml) per cm$^2$ of substrate surface area, at 3000rpm for 1min30s.
6.4.2. PPL of DTMS on Oxidised Silicon

A Sc(OTf)$_3$ dip-coated or spin-coated oxidised silicon substrate was mounted on the AFM stage. A PDMS PPL array was oxidised by oxygen plasma cleaning for 3 minutes at high setting, then mounted on a custom holder. The PDMS face of the mounted array was suspended in ethanol and sonicated for 3 minutes. Care was taken not to wet the holder with ethanol. The array was then dried with N$_2$ and mounted on the AFM head. Alignment of the PPL array with the substrate was then performed using an automated procedure described in literature$^{51}$. The array was then removed from the AFM and placed on a level platform. 20µL of dodecyltris(2-methallyl)silane (145mg, 0.4mmol) in ethanol (20ml) was applied to the face of the array using a micropipette. Once the ethanol had evaporated ($\geq$30min) the PPL array was mounted on the AFM head. The array was oscillated vertically with modulations of ±5.39µm and approached to the substrate by raising the stage. Once the desired contact force was observed on extension of the array towards the surface (1-3µN), oscillation was stopped. Lithography was then performed with equivalent vertical movements of the array (+5.39µm when contacting the surface, -5.39µm when withdrawn from the surface). Following lithography the substrate was removed from the stage, placed in a closed petri dish and permitted to develop for 1-48h. The substrate was then cleaned by sonication in acetone (50ml) for 15min, then rinsed by submersion in methanol (50ml). Full lithography conditions can be found in tables 2 and 3, section 3.2. The conditions used in the control experiments can be found in table 4, section 3.2.

6.5. Surface Functionalisation Methods for R-Sc(OTf)$_2$ Localisation

6.5.1. Substrate A

A glass desiccator, glass cuvette and glass syringe with needle were dried overnight in an autoclave at 90°C. The cuvette, syringe and needle were then placed in the desiccator. The desiccator was flushed with nitrogen and allowed to cool to room temperature. Silicon
substrates were cleaned by sonication in acetone (50ml) for 15 minutes then rinsed by submersion in methanol (50ml) and dried with N₂. The substrates were oxygen plasma cleaned for 3 minutes at high setting then transferred directly to the nitrogen flushed desiccator. The glass syringe was flushed with nitrogen and used to transfer 3-mercaptopropyltrimethoxysilane (100µl, 0.53mmol) to the glass cuvette in the desiccator. The desiccator was then sealed and vacuum was established using a vacuum line. After 24 hours the substrates were removed from the desiccator and cleaned by sonication in acetone (50ml) for 15 minutes, then rinsed by submersion in methanol (50ml) and dried with N₂.

6.5.2. Substrate B

Oxone® (2.1g, 6.83mmol) and NaHCO₃ (675mg, 8.03mmol) were dissolved in a mixture of water (120ml) and CH₃CN (180ml). A magnetic stirrer and hotplate was used to mix the solution at 40°C in a large glass beaker to dissolve the reagents. Once the solution had cooled a small glass petri dish was placed in the solution at the centre of the beaker. The magnetic stirring rod was placed within the petri dish. Substrate A was submerged in the solution at the periphery of the beaker with the functionalised face pointing upwards. This setup is illustrated in figure 16. The petri dish was included to prevent the magnetic stirring rod from contacting and damaging the substrate. Caution was taken to ensure that the functionalised face of the substrate did not contact any surfaces. The solution was gently stirred with the magnetic stirrer for 36h. The substrate was then cleaned by sonication in water (50ml) for 10 minutes followed by sonication in acetone (50ml) for 10 minutes, rinsing by submersion in methanol (50ml) and drying with N₂.
Figure 16. Apparatus setup for application of reagent solutions to substrates. The petri dish was included to prevent contact of the magnetic stirring rod with the substrates.

6.5.3. Substrate C

The same apparatus setup was used as in section 6.5.2. (figure 16) but a different substrate and reagent solution were used. Substrate B was submerged in a solution of ScCl$_3$ (454mg, 3mmol) in H$_2$O (300ml) with gentle stirring for 24 hours. The substrate was cleaned by sonication in acetone (50ml) for 15 minutes, rinsed by submersion in methanol (50ml) and dried with N$_2$.

6.5.4. Substrate D

TfOH (100µl, 1.13mmol) was added dropwise to water (100µl) using a glass pipette. This solution was applied to the face of substrate C in a glass vessel using a glass pipette. After 1 hour the acid was diluted by slow addition of water, neutralised by addition of excess NaHCO$_3$ with gentle stirring using a glass rod, and left for 1 hour before disposal of the solution. The substrate was cleaned by sonication in water (50ml) for 10 minutes followed by sonication in acetone (50ml) for 10 minutes, rinsing by submersion in methanol (50ml) and drying with N$_2$. 
6.5.5. Substrate E

The same apparatus setup was used as in section 6.5.2. (figure 16) but a different substrate and reagent solution were used. Substrate B was submerged in a solution of Sc(OTf)$_3$ (744mg, 1.51mmol) in water (300ml) with gentle stirring for 24 hours. The substrate was cleaned by sonication in acetone (50ml) for 15 minutes then rinsed by submersion in methanol (50ml) and dried with N$_2$.

6.5.6. Functionalisation of PPL Arrays

The procedures described in sections 6.5.1., 6.5.2. and 6.5.5. were sequentially performed using a PPL array in place of silicon wafer. Caution was taken not to contact the PDMS face of the array with any surfaces. Ethanol was used in place of acetone in all washing steps.
References


38. Eichelsdoerfer, D. J. et al. Large-area molecular patterning with polymer pen lithography.


