

## **Rapid, Metal-free Hydrosilanisation Chemistry for Porous Silicon Surface Modification**

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**Supporting Information**

## Table of Contents

pSi fabrication	3
Hydrosilane grafting procedure	3
Analytical techniques	3
<b>Figure S1</b> XPS C1s spectrum	5
<b>Figure S2</b> SEM of pSi surfaces	6
<b>Figure S3</b> ToF-SIMS total positive ion image for pSi MPs	7
References	8

**pSi fabrication:***pSi films*

Three different types of pSi films were prepared:

3 – 6  $\Omega\text{cm}$ , p-type silicon (Siegert) was etched in 1:1 HF(48 %):ethanol at 20 mA/cm<sup>2</sup> for 5 min. The etched surface was washed with ethanol and acetone, dried under N<sub>2(g)</sub> and used immediately for subsequent functionalisation procedures.

0.008 – 0.0012  $\Omega\text{cm}$ , p-type silicon (Siltronix) was etched in 1:1 HF(48 %):ethanol at 15 mA/cm<sup>2</sup> for 30 min. The etched surface was washed with ethanol and acetone, dried under N<sub>2(g)</sub> and used immediately for subsequent functionalisation procedures.

< 0.002  $\Omega\text{cm}$ , p-type silicon (Siegert), was firstly etched in 3:1 HF(48 %):ethanol at 166.67 mA/cm<sup>2</sup> for 30 s and the porous layer was dissolved in 5 M NaOH to remove the parasitic layer. A working etch on the prepared surface was then performed in 3:1 HF(48 %):ethanol at 166.67 mA/cm<sup>2</sup> for 10 min. The etched surface was washed with ethanol and acetone, dried under N<sub>2(g)</sub> and used immediately for subsequent functionalisation procedures.

*pSi microparticles*

pSi microparticles were fabricated from p-type Si wafers (resistivity < 0.001  $\Omega\text{cm}$ ) (Siegert) in an 18 cm<sup>2</sup> etching cell in 3:1 HF/ethanol solution with a current density of 222 mA cm<sup>-2</sup> for 4 min, and then electropolished for 30 s at 500 mA cm<sup>-2</sup>. The freestanding porous layer was fractured into microparticles using 20 min of sonication in ethanol (Soniclean 160HT, 70 W, Soniclean Pty. Ltd., Thebarton, Australia) to transform any large sheets of pSi into smaller particles for recovery. The resulting particles were sieved into different size fractions and particles in the sub 25  $\mu\text{m}$  size range were used for ToF-SIMS analysis.

**Hydrosilane grafting procedure:**

An oxidised pSi surface was added to a solution of hydrosilane (60 mg) and catalyst (2.5 mg) in 5 mL of dichloromethane (DCM). The reaction was allowed to proceed in a closed vessel with agitation at room temperature for a time of 2 – 10 min, after which the surface was removed and washed with copious amounts of DCM and dried under a stream of N<sub>2(g)</sub>.

**Analytical techniques:***Infrared spectroscopy*

IR spectra were recorded on a Bruker Hyperion 1000 IR microscope using transmission mode. Spectra were recorded over the range of 650 – 4000 cm<sup>-1</sup>, with a clean flat silicon wafer of the same type used as a background. All spectra were recorded as an average of 64 scans at a resolution of 4 cm<sup>-1</sup> and were analysed using Opus (v7.2) software (Bruker). All IR spectra were normalised to the Si-O peak. Low resistivity (IR transparent) pSi was used to perform transmission IR measurements in order to avoid interference fringes that are observed when performing diffuse reflectance IR (DRIFT) on pSi surfaces.

*Water contact angle measurements*

Water contact angle measurements were conducted using a custom-built goniometer, with a Panasonic CCTV camera (WV-BP550/G) to capture the drop-surface images. A 1  $\mu\text{L}$  drop of ultrapure MilliQ water was deposited onto each surface using a 10  $\mu\text{L}$  syringe. A photograph was immediately captured and contact angles were determined using ImageJ (v1.44p) with the Drop Analysis plugin. Surface contact angles were taken as an average of five replicate measurements per surface.

### *X-ray photoelectron spectroscopy*

Two XPS instruments were used to analyse the prepared samples.

XPS spectra were recorded on a Specs SAGE XPS spectrometer using Mg  $K\alpha$  radiation source ( $h\nu = 1253.6$  eV) operating at 10 kV and 20 mA. A survey spectrum was recorded over the energy range 0 – 1000 eV using a pass energy of 100 eV and resolution of 0.5 eV using a take-off angle of  $90^\circ$  with respect to the sample surface. The areas under the photoelectron peaks in the spectrum were used to calculate the percentage atomic concentrations. High resolution spectra (0.1 eV) were recorded for the C1s photoelectron peak at a pass energy of 20 eV. The binding energies were referenced to the C1s neutral carbon peak at 285 eV, to compensate for the effect of surface charging. A spot size of 3 mm was used. The processing and de-convolution of the high-resolution spectra were performed using CasaXPS software.

The second XPS instrument used was a Kratos Axis Ultra with DLD. The x-ray was a monochromatic aluminium x-ray running at 225 W with a characteristic energy of 1486.6 eV. The area of analysis (Iris aperture) was a 0.3 mm x 0.7 mm slot; the analysis depth was approximately 15 nm into the surface of the sample. The analysis vacuum was  $4 \times 10^{-9}$  Torr. The electron take off angle was normal to the sample surface. Survey spectra were collected over the range of -10 – 1110 eV using a pass energy of 160 eV and a resolution of 0.5 eV. High resolution spectra (0.1 eV) were collected for the C1s photoelectron peak at a pass energy of 20 eV. Spectra were interpreted using the software package CasaXSP.

### *ToF-SIMS*

ToF-SIMS measurements were performed using a Physical Electronics Inc. PHI TRIFT V nanoToF instrument (Chanhassen, MN, USA) equipped with a pulsed liquid metal Au<sup>+</sup> primary ion gun (LMIG), operating at 30 kV. The extractor current of the ion source was maintained at 3  $\mu$ A. Positive ion ToF-SIMS images (100  $\mu$ m  $\times$  100  $\mu$ m) were acquired on the blank (oxidised) and DMPS functionalized pSi films and micro-particles using ‘unbunched’ Au1 beam settings to deliver optimised spatial resolution. Positive ion mass spectra were acquired on the same surfaces using a ‘bunched’ Au1 beam setting for optimal mass resolution. The acquisition time for both images and spectra was 5 min each. Mass calibration of the spectra was done with CH<sub>3</sub><sup>+</sup>, C<sub>2</sub>H<sub>5</sub><sup>+</sup>, and C<sub>3</sub>H<sub>7</sub><sup>+</sup> ions. Experiments were performed at high vacuum ( $< 10^{-8}$  Torr), in static mode (i.e., below  $10^{12}$  ions/cm<sup>2</sup>) to minimise sample damage.

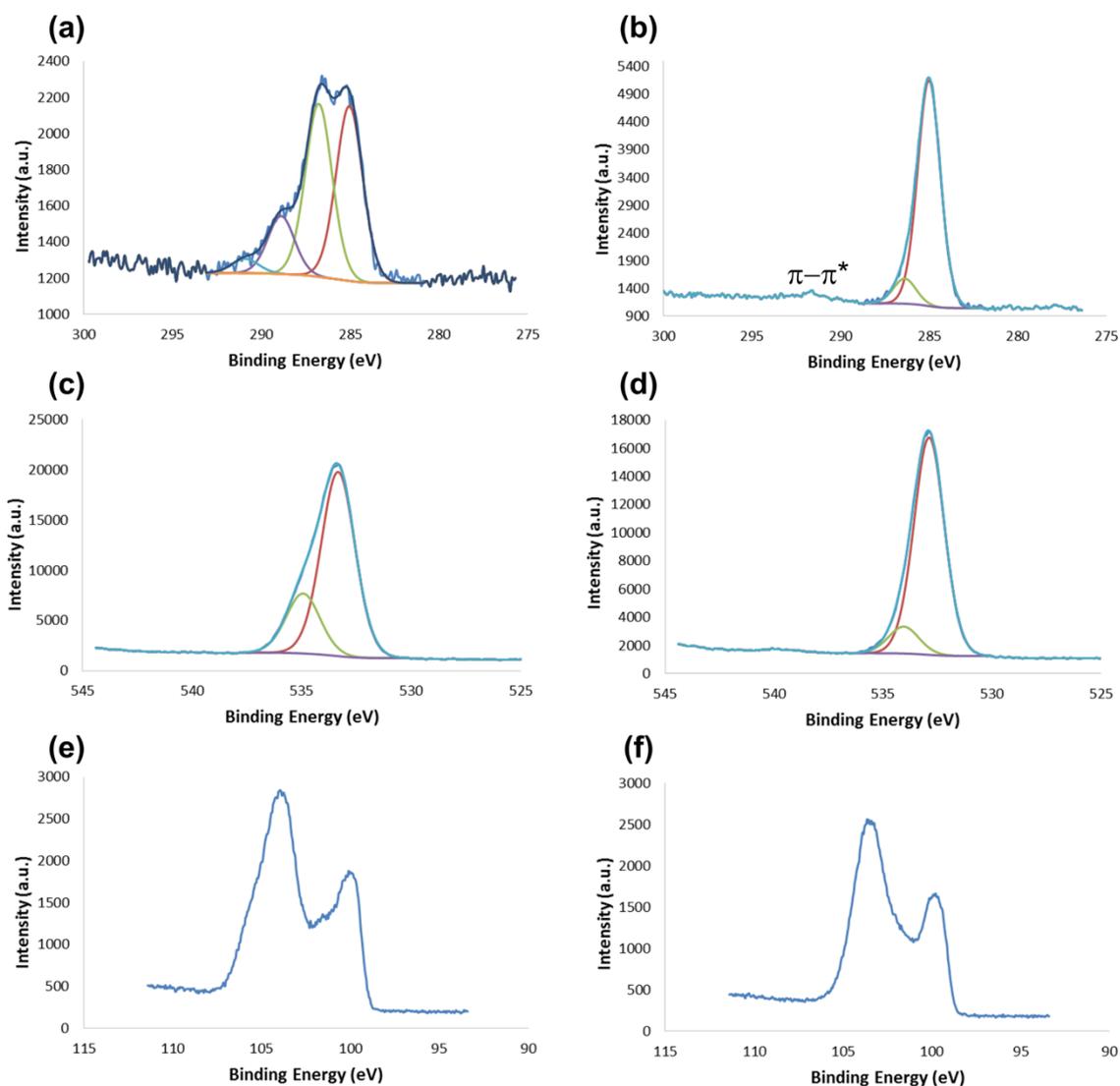
### *SEM*

Scanning electron microscopy (SEM) was performed on a Crossbeam 540 SEM (Zeiss, Germany). An accelerating voltage of 3 kV and an ‘in-lens’ detector were used to view the pSi surface, at a working distance of 2 mm. The pSi film was cut to reveal a clean edge before being clamped into a vertical conductive aluminium stub and remained uncoated for analysis.

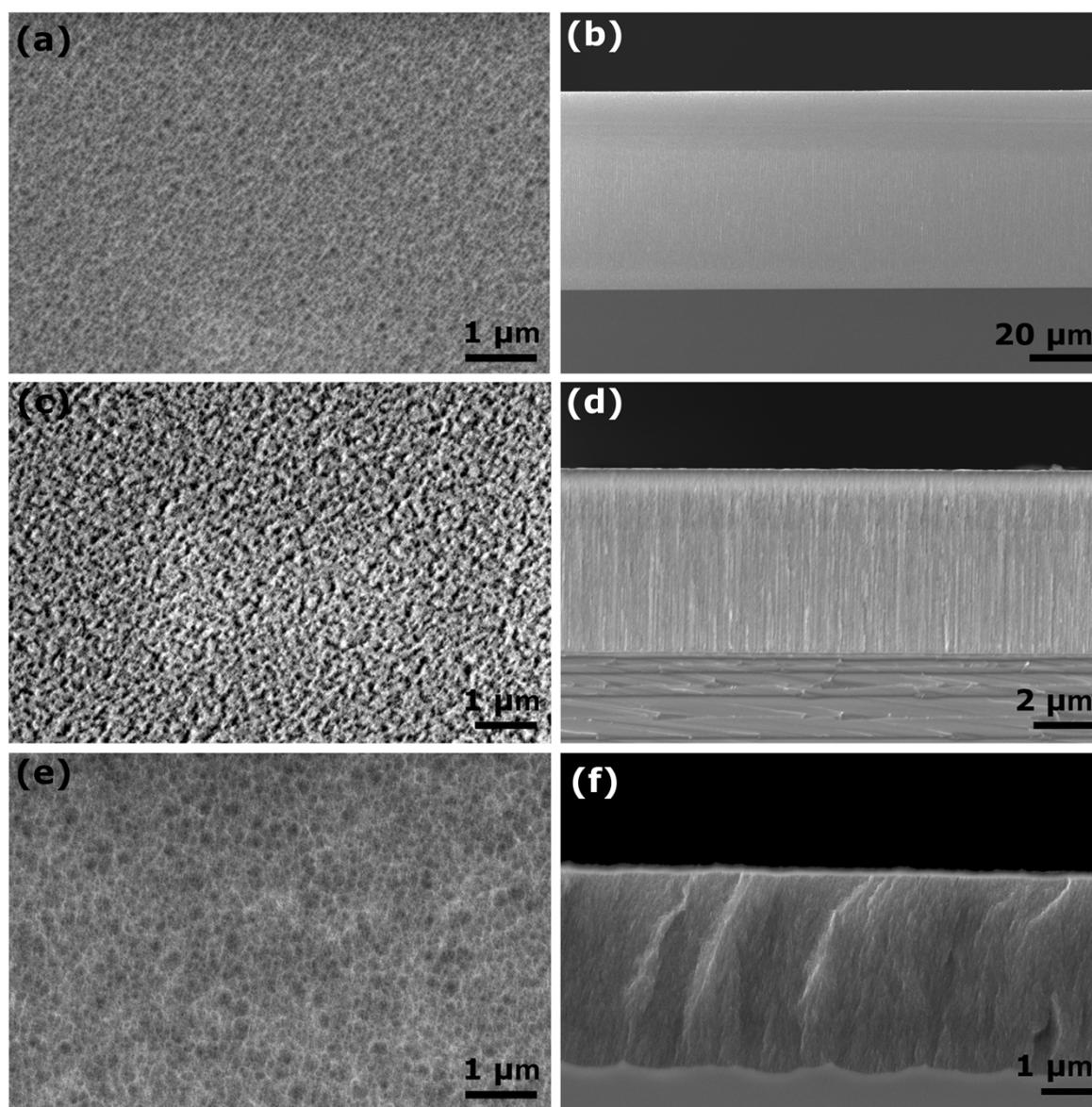
### *SALDI-MS*

A certified standard of methadone (1 mg/mL) was supplied from Forensic Science South Australia. Stock solutions of methadone at 0.01 mg/mL in ethanol were prepared and stored at -20 °C. Working solutions of methadone at 1  $\mu$ g/mL in milliQ water were made from the stock solution. Methadone (1  $\mu$ g/mL, 1  $\mu$ L) was pipetted onto the functionalised pSi chip and allowed to dry. The pSi chip was adhered to a modified MALDI stainless steel target plate (MSP 384) using double sided conductive carbon tape and analysed using mass spectrometry.

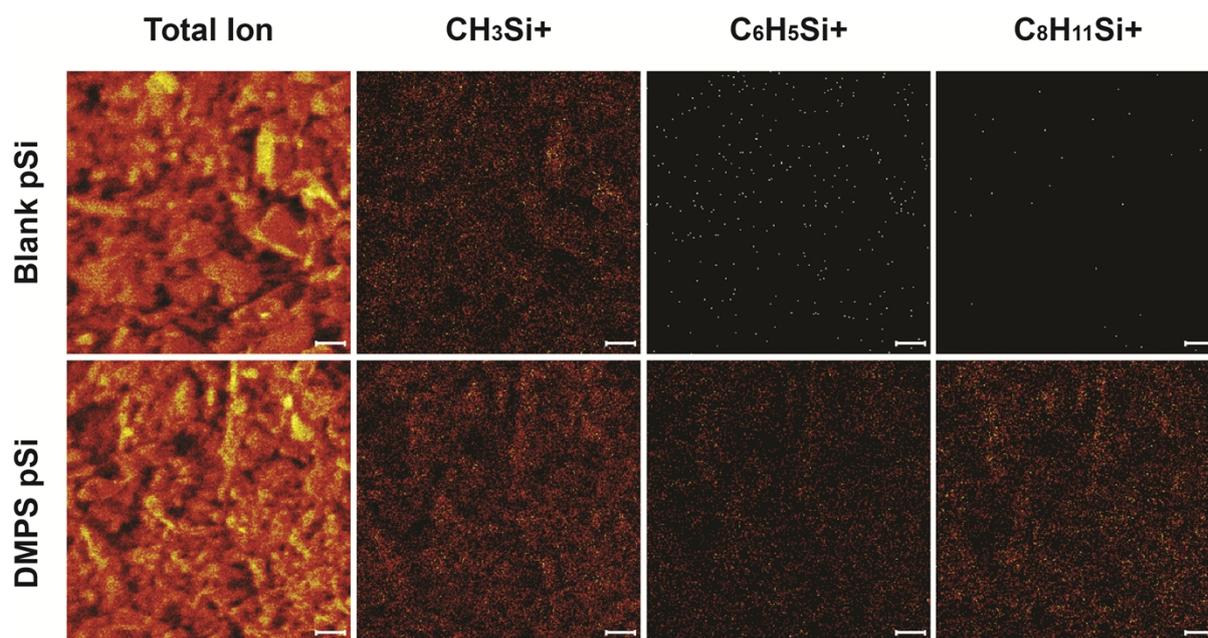
An UltrafleXtreme MALDI-TOF-TOF mass spectrometer (Bruker Daltonics) equipped with a SmartBeam (337 nm, Nd:Yag) 2 kHz pulsed laser was used to collect mass spectra for methadone. The mass spectrometer was operated in reflectron positive mode with a laser attenuator offset of 1 %. Mass spectra were generated by averaging 500 individual laser shots. Data acquisition used flexcontrol 4.0 software and data analysis was performed using flexAnalysis version 3.3. Quadratic external calibration of the TOF tube was performed prior to each acquisition using the peaks for Cs<sup>+</sup> (m/z 132.90490), Cs<sub>2</sub>I<sup>+</sup> (m/z 392.71483), Cs<sub>3</sub>I<sup>+</sup> (m/z 652.52475) and Cs<sub>4</sub>I<sup>+</sup> (m/z 912.33468).



**Fig. S1** Deconvoluted high resolution C1s and O1s along with Si2p XPS spectra for ozone oxidised (a, c, e) and DMPS-modified (b, d, f) pSi surfaces. The ozone oxidised pSi C1s XPS spectrum (a) shows minimal carbon content arising from adsorbed hydrocarbons. The DMPS C1s spectrum (b) shows a prominent peak at 285.0 eV, corresponding to the carbon bonding present in the phenyl group and a small peak at 286 eV for C-O bonds, arising from adsorbed hydrocarbons.<sup>1</sup> A small  $\pi$ - $\pi^*$  satellite peak at 291.8 eV from the phenyl group is also observed. The O1s spectra displays a prominent peak at 533.0 eV corresponding to Si-O<sub>x</sub> bonds on the surface for both ozone (c) and DMPS (b) modified pSi, along with a peak at 535.0 eV that is more pronounced in the ozone oxidised surface, corresponding to adsorbed water and hydrocarbons.<sup>2</sup> The Si2p spectra for ozone and DMPS modified pSi (e and f respectively), show characteristic peaks at 100 eV and 103 eV, corresponding to Si bonds and Si-O bonds, respectively, for both surface modifications.



**Fig. S2** Top down and cross-sectional SEM images of the pSi surfaces used for (a, b) ToF-SIMS analysis, (b, c) contact angle, XPS and SALDI-MS and (e, f) IR analysis. The surfaces are imaged post oxidation and prior to hydrosilanisation. The pSi surface for ToF-SIMS analysis is 61.8 μm thick, which correlates to the depth of the positive ion signal observed in the ToF-SIMS analysis of the DMPS functionalised pSi surfaces.



**Fig. S3** ToF-SIMS images (100  $\mu\text{m}$  x 100  $\mu\text{m}$ ) for the total positive ions and for the positively charged fragments CH<sub>3</sub>Si<sup>+</sup>, C<sub>6</sub>H<sub>5</sub>Si<sup>+</sup> and C<sub>8</sub>H<sub>11</sub>Si<sup>+</sup> characteristic of DMPS acquired on the ozone oxidised pSi and DMPS functionalised pSi MPs. Scale bar on the images = 10  $\mu\text{m}$ .

**References:**

- 1 M. Y. Bashouti, Y. Paska, S. R. Puniredd, T. Stelzner, S. Christiansen and H. Haick, *Physical Chemistry Chemical Physics*, 2009, **11**, .
- 2 A. Thøgersen, J. H. Selj and E. S. Marstein, *Journal of The Electrochemical Society*, 2012, **159**, D276.