Electronic Supplementary Material (ESI) for Analyst.

Supporting Information

Surface-assisted laser desorption/ionization mass spectrometry using ordered silicon nanopillar arrays

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- Materials and methods section for the fabrication of DIOS substrates.
- Figure S-1 containing the FTIR spectrum referred to in the main text from a SiNP substrate.
- Figure S-2 containing a SALDI-MS spectrum collected from a SiNP array with 450 nm length and 450 nm nanopillar diameter, etched with 0.1 M H_2O_2.

- Table S-1 containing S/N values from the SALDI-MS analysis of peptides. The table shows the S/N for each peptide collected from SiNP arrays with varying lengths.
- Figure S-3 containing a SALDI-MS spectrum collected from a SiNP array with 450 nm length and 450 nm diameter, etched with 0.1 M H_2O_2. The spectrum shows the peaks collected from a methadone spiked analyte with a mass range from 0 to 340 m/z.
- Figure S-4 containing water contact angle measurements (WCA) on SiNP arrays with and oxidized and fluorosilane functionalized surfaces.
- Figure S-5 containing SALDI-MS spectra of methadone and its metabolite EDDP in clinical samples of urine, blood, and saliva collected from patients undergoing methadone treatment.
- Table S-2 containing S/N values of methadone and EDDP collected from clinical urine, blood, and saliva samples from patients undergoing methadone treatment. The values depict S/N collected from SiNP arrays and DIOS substrates.

Materials

HF (48 %) was obtained from Fischer Scientific (United Kingdom). Ethanol (EtOH) (100 % undenatured), methanol (99.9 %), acetone and DCM were purchased from Chem Supply (Australia). Water was purified using a Labconco water purifier (USA) (referred to as MilliQ water). Tridecafluoro 1,1,2,2 tetrahydrooctyldimethylchlorosilane (F13) was purchased from Gelest Inc (USA). α-Cyano-4-hydroxycinnamic acid (CHCA) was purchased from Bruker-Daltonics (Germany).

Experimental

Monocrystalline (0.008-0.02 Ω.cm) antimony doped n-type Si (100) wafers from Silicon Quest International (CA, USA) were cut with a diamond cutter into 3.5 cm x 3.5 cm squares. The cleaning processes were carried out by sonicating the wafers in 99.9 % methanol and drying under a stream of nitrogen. The pSi arrays were fabricated by light-assisted anodic etching of cut Si wafers using a photomask. In brief, the wafers were clamped into a custom-built Teflon anodization cell contacting a gold foil anode (Space Products International, CA, USA). A 0.5 mm diameter platinum wire (99.9 %, Aldrich, WI, USA) formed into a ring was used as a cathode. A 1:1 HF:EtOH electrolyte solution was filled into the Teflon well. The Si surface was illuminated using a fiber optic light source which passed through a photomask and then through a set of two aspheric lens, f = 80 mm (OptoSigma, CA, USA) for collimation. A constant current of 3.2 mA/cm^2 was then applied across the cell for 2 min using a source meter program, created in LabView 6.1 to control a 2425 current

source meter (Keithley, Ohio, U.S.A). The pSi surfaces were then subjected to several methanol washes, before being dried under a stream of nitrogen gas.

The freshly-etched pSi was ozone-oxidized at a flow rate of 3.25 g/hr using an Ozone-Generator 500 (Fischer, Germany). Following oxidation, the wafer was subjected to a second pore broadening etch using 5 % HF/H2O for 30 s. Subsequently, the double etched surface was ozone oxidized (as above) for a second time. The hydroxyl-terminated surface was then silanized via the addition of 80 μL of neat F13 for 15 min at 90 ˚C. After silanization, the pSi arrays were washed with methanol, dried under a stream of nitrogen and then stored in a desiccator until required.

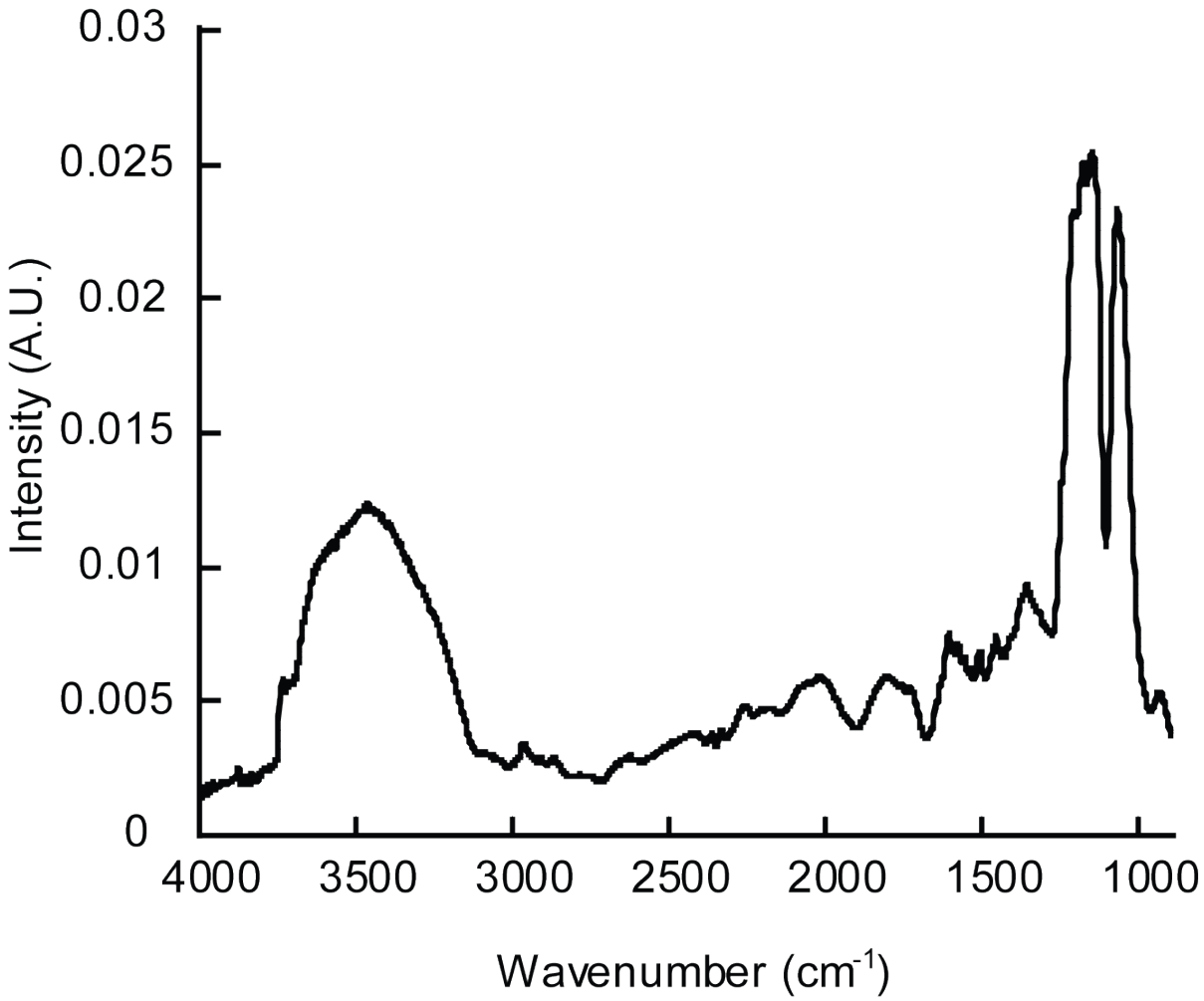

Figure S1. FTIR spectrum collected using Diffuse Reflectance Infrared Fourier Transform (DRIFT) on SiNP arrays. The SiNP array was taken after fabrication directly without any further modification and analyzed. In the sample spectrum, Si-O-Si and Si-OH characteristic peaks can be observed at 1050-1200 and 3745 (cm^{-1}), respectively. Additionally, a broad peak characteristic of bonded -OH was present between 3100 and 3600 cm^{-1}.

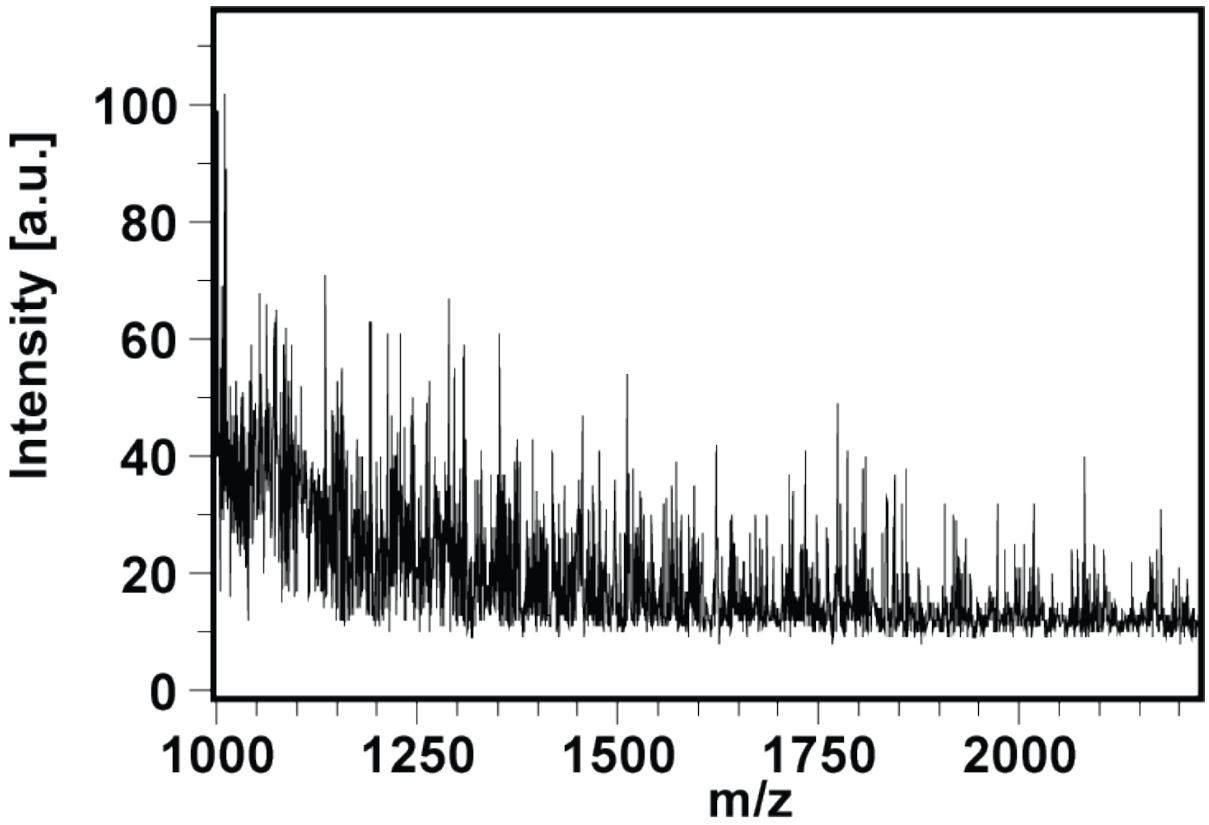

Figure S-2. SALDI-MS spectrum collected of a MilliQ water droplet that did not contain any peptides. The substrate used was a SiNP array etched for 1 min using a solution of 4.8 M HF/0.1 M H_2O_2.

Table S-1. Signal-to-noise values for peptides measured on SiNP arrays that were etched for varying durations of time.

		Duration for the etching reaction of the SiNW arrays using a solution of 4.8 M HF/ 0.1 M H_2O_2		
Peptide	Molecular weight (Da)	1 min	5 min	20 min
Angiotensin II	1047.19	7.8	11.5	4.7
Angiotensin I	1297.49	36.2	20.9	6.8
Substance P	1348.64	55.6	29.1	5.0
Bombisin	1620.86	15.8	6.2	n.d
ACTH clip 1-17	2094.43	4.2	n.d	n.d
ACTH clip 18-39	2466.68	5.5	n.d	n.d
Somatostatin	3149.57	5.4	n.d	n.d

This table shows the signal-to-noise values obtained from SiNP arrays that were etched in a solution of 4.8 M HF/ 0.1 M H_2O_2 for 1 min, 5 min, and 20 min respectively. The table shows the peptide name, its molecular weight, and S/N ratios on each SiNP array for each peptide in the peptide mix. n.d refers to 'no detection' or in other words, negligible signal that did not qualify as a detection. S/N values that are ≥3 are considered as a successful detection.

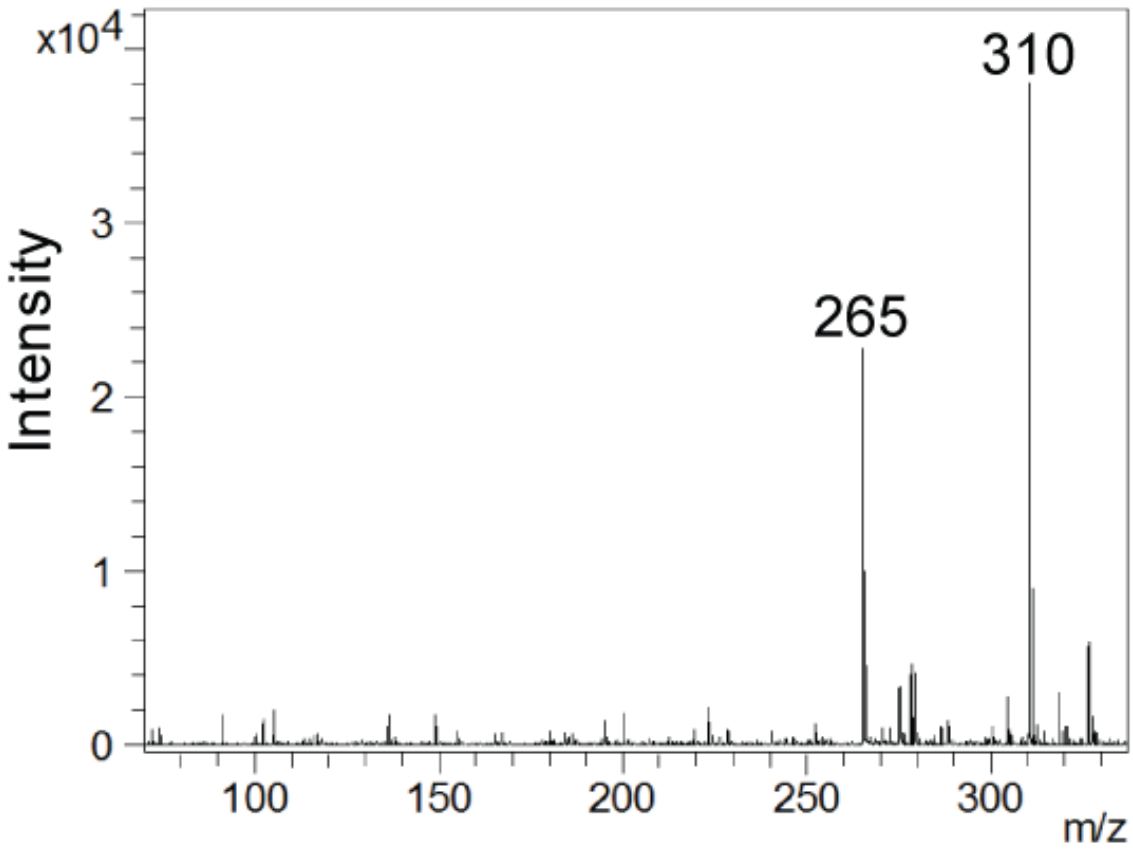

Figure S-3. Representative SALDI mass spectra on SiNP arrays etched in a 4.8 M HF/0.1 M H_2O_2 solution for 1 min (450 nm in length, 450 nm diameter, 100 nm inter-nanopillar spacing, and an aspect ratio of 1.0) for methadone with a MH+ = 310 m/z. Another peak appearing at 265 m/z was identified as a methadone fragment.

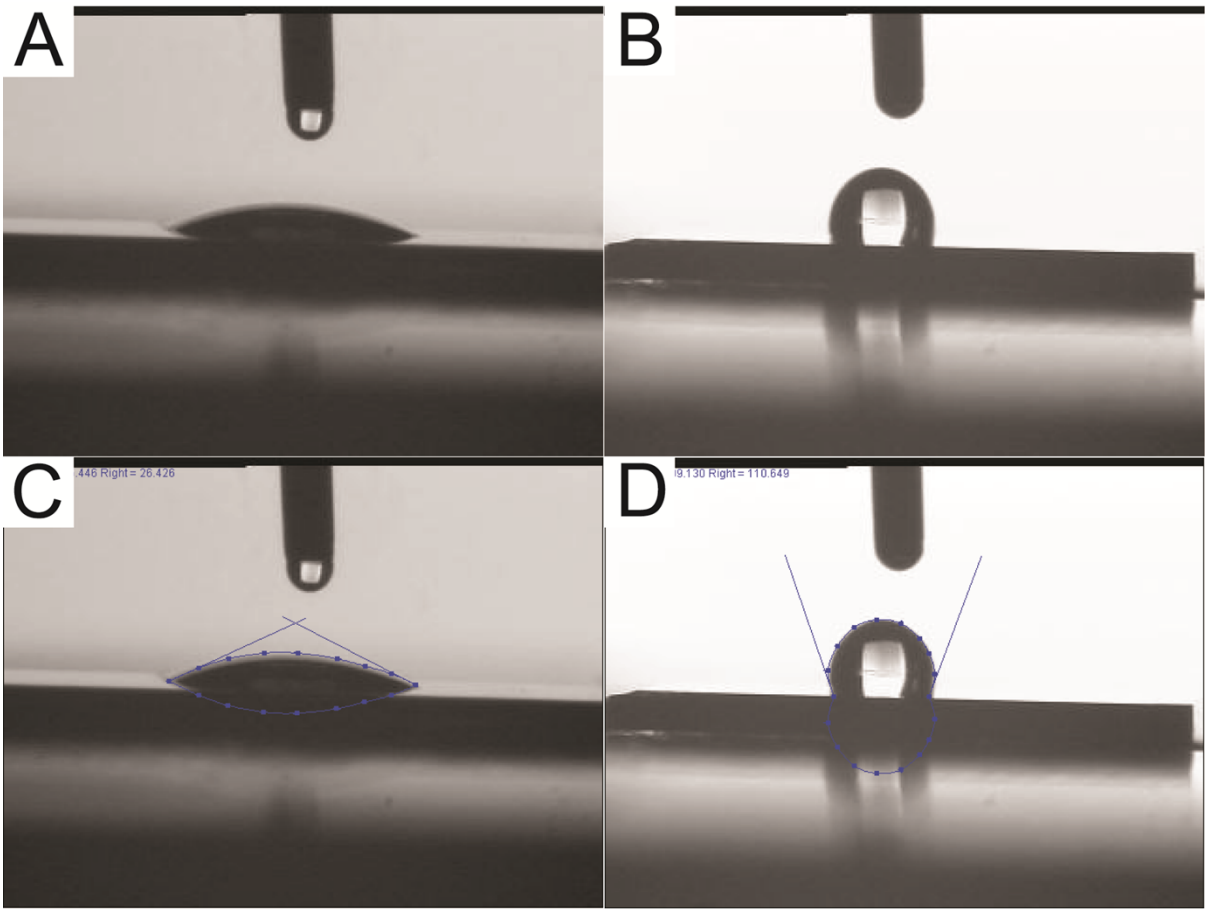

Figure S-4. Optical images of water droplets (10 µL) deposited on SiNP arrays with different surface functionalities. A) SiNP array that was oxidized by exposure to ozone for 30 min. B) SiNP array that was oxidized by exposure to ozone, followed by a neat silanization reaction using (Tridecafluoro-1,1,2,2-tetrahydrooctyl) dimethylchlorosilane (F_{13}) at 95 ˚C for 30 min. C) depicts computer software measurement of the water contact angle (WCA) on the SiNP array from A). WCA was measured at 25˚ ± 1˚. D) depicts computer software measurement of WCA on SiNP array from B). WCA was measured at 110˚ ± 1˚.

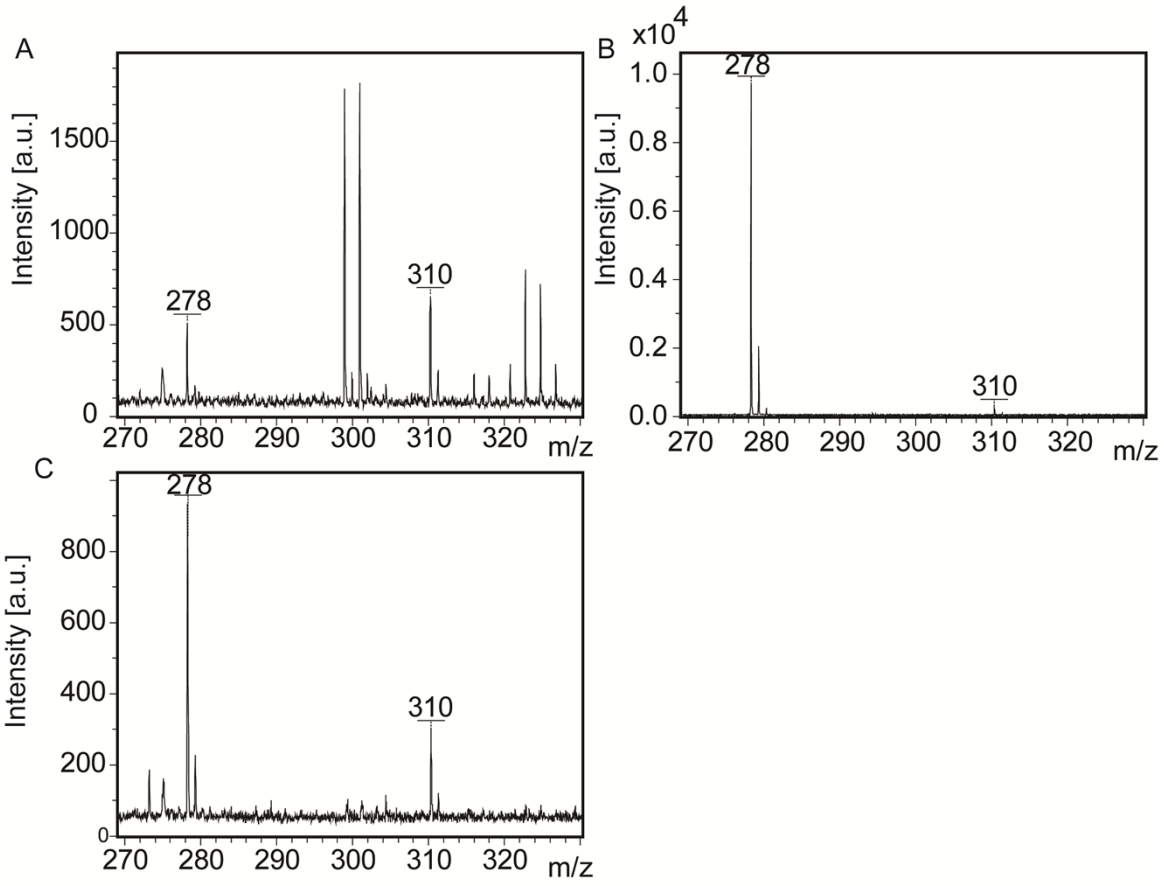

Figure S-5. SALDI-MS spectra of methadone (310 m/z) and its metabolite EDDP (278 m/z) detected in clinical samples composed of A) urine, B) blood, and C) saliva collected from patients undergoing methadone treatment. Spectra were collected on SiNP arrays etched in 4.8 M HF and 0.1 M H_2O_2 to form SiNPs with 450 nm diameter, 450 nm length, and 1.0 aspect ratio. The SiNP arrays were functionalized with a fluorosilane (F_{13}).

Table S-2. Tabulated S/N values for methadone and EDDP collected from clinical samples of urine, blood, and saliva on SiNP arrays and DIOS substrates using SALDI-MS. Both SiNP arrays and DIOS substrates were functionalized with a fluorosilane (F13).

	SiNPs		**DIOS**	
	Methadone (310 m/z)	EDDP (278 m/z)	Methadone (310 m/z)	EDDP (278 m/z)
Urine	16.23	867	56.17	554.93
Blood	8.6	34.9	n.d	40
Saliva	7.6	13.7	9.4	21.3