Supporting Information

Experimental section for the fabrication of the SiO_2 nanowires and their conjugation with monofunctional silanes.

Materials

The metals for e-beam evaporation and device fabrication (99.999% or greater purity) as well as the FABMATE e-beam crucibles were purchased from Kurt Lesker and used according to the manufacturer's instructions. Photoresists for optical lithography were acquired from Rohm and Haas (Shipley 1805), AZ Electronic Materials (AZ1518), MicroChem (LOR1A and LOR3A), and stored at 4C before use. All buffered oxide etch (BOE), TMAH, and rinsing solvents were acquired from J.T Baker. 3-aminopropyldimethylethoxysilane (APDMS) for the monolayers was purchased from Gelest, Inc. and stored under vacuum desiccation until used. Triethylamine (TEA) was purchased from Sigma-Aldrich and used as received.

Device Fabrication

The fabrication of the SiO2-based, accumulation mode silicon nanowire and nanoplate devices has been described previously.[1] Briefly, the process flow starts with bonded silicon-on-insulator (SOI) wafers (SOITEC) with a buried oxide thickness of 1450Å and a top silicon thickness of 550Å. The top silicon is dry oxidized at 1050C, then wet etched in 10:1 BOE to thin the silicon layer to 300Å. Afterwards, the nanowire patterns are defined with e-beam lithography using a PMMA/LOR1A resist layer, and chrome evaporated on top with a subsequent lift-off to form the first hard mask. The nanoplates and other larger features are then defined using optical

lithography, with a second evaporation of chrome and lift-off to form another hard mask. Finally, a TMAH etch of the exposed silicon layer is performed to define the active silicon devices, with a removal of the chrome hard mask using CR-14 etchant (CYANTEK Corp.). The source and drain regions were then boron-doped via ion implantation (simulations show ~1019/cm2) using a 1um thick photoresist mask. Dry oxidation to form the SiO2 gate dielectric, as well as simultaneous dopant activation, was performed at 1050C in a vertical furnace to a thickness of ~175 Å (confirmed by AFM step height analysis). Following oxidation, a forming gas anneal at 400C in 5%H2/N2 was performed to passivate interface traps and dangling bonds. Via holes were etched into the contact regions, followed by patterning of 250ÅTi/750Å Pt to make the metal contacts to the source/drain regions of the devices. A 550C rapid thermal anneal was then performed to lower the contact resistance. Afterwards, a 4000Å thick PECVD silicon nitride passivation layer was deposited over the wafer. Optical lithography was used to define the release window areas for the devices and CF4 reactive ion etching (90W, 35mTorr, 60sccm) with subsequent 50:1 BOE to etch the underlying passivation layer and release the devices for testing. Finally, the devices undergo a second forming gas anneal to alleviate any RIE induced gate oxide damage.

Monolayer Formation and Bioconjugation

The formation of 3-aminopropyldimethylethoxysilane (APDMS) monolayers on the nanowire surfaces has also been described in previous literature.[2] Briefly, the devices were cleaned in a H2SO4:H2O2 solution (7:3) for 30mins, then in a 300W O2 plasma at 500mTorr for 1 minute. The devices were placed in a septum vial, modified with a well for the silane solution and flushed with N2, then evacuated to a pressure of 10 Torr. A solution of APDMS/1% TEA (v/v) was then injected via hypodermic needle into the well and the vial place in a convection oven at

100C overnight. The devices were rinsed with acetone and methanol, then blown dry with N2 gas and stored in a vacuum desiccator until use.

Supplementary Figures and Tables

Etching Regime	Etch Rate (nm/min)	Std. Dev (nm/min)
Region 1 (SiN)	78.2	2.3
Region 2a (Pt)	0.2	1.9
Region 2b (SiO_2)	19.6	1.8

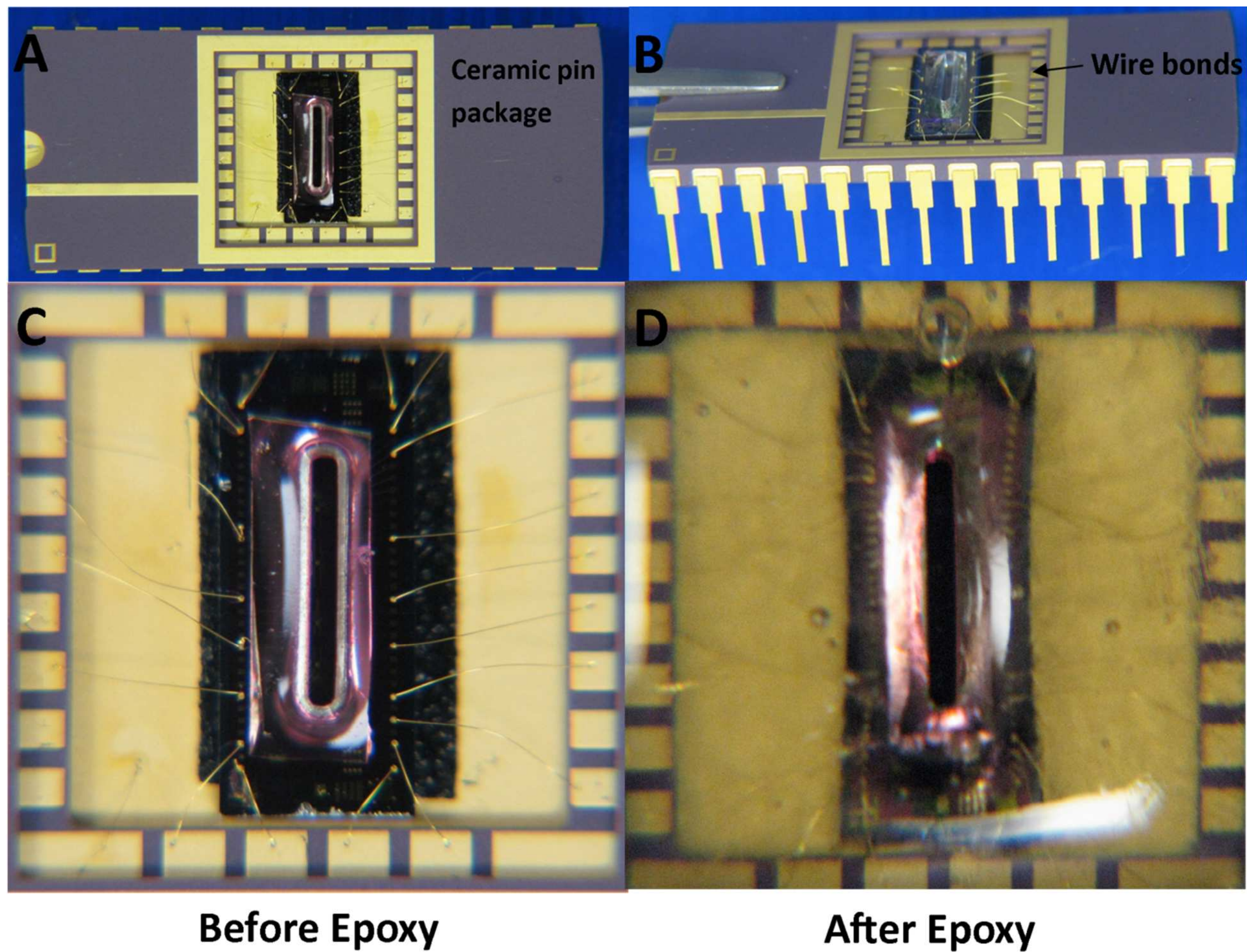
Table S1. Table of extracted etch rates and standard deviations of CF_4 based RIE etching for silicon nanowire device release.

Linker	Goat anti-Mouse IgG Fluorescence (A.U)	Goat anti-Mouse IgG Fluorescence (Normalized)	ΔVt (V)	ΔVt (V) (Normalized)
DSC	120.10 (2.34)	1.0000	-0.720 (0.012)	1.000
BS(PEG)	98.10 (2.21)	0.8169	-0.646 (0.006)	0.897
glutaraldehyde	77.93 (6.16)	0.6489	-0.608 (0.010)	0.845
APDMS	10.02 (0.05)	0.0834	-0.258 (0.003)	0.358

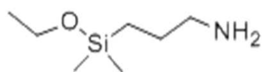
Table S2. Table of values for primary antibody adsorption fluorescence and electrical response on the silicon nanowire FET's.

Linker	Mouse IgG (A.U)	Rabbit IgG (A.U)	Mouse IgG/Rabbit IgG Binding Ratio	Mouse IgG binding capacity (% coverage)
DSC	97.74 (3.55)	18.61 (0.91)	5.252	81.38%
BS(PEG)	78.83 (3.83)	3.084 (0.95)	25.563	80.36%
glutaraldehyde	61.27 (2.34)	36.33 (3.66)	1.687	78.63%
APDMS	6.34 (0.08)	6.84 (0.09)	0.927	63.28%

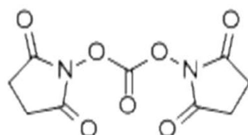
Table S3. Table of fluorescence values of goat anti-mouse IgG binding affinity towards mouse IgG and rabbit IgG for the different linker chemistries.



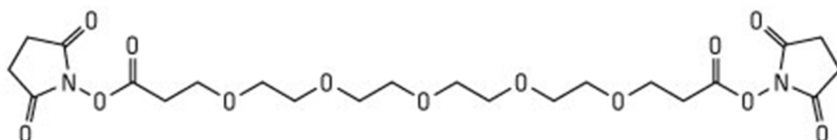
Supplementary Figure 1. Pictures of silicon nanowire array device inside a ceramic pin package wired bonded (A), with a tilted picture illustrating the wire bonds in (B). A close up image of the center of the package is in (C). The image shows the conducting carbon tape which holds the chip to the package, the wire bonds attaching the device leads to the package outside, and the PDMS well bonded to the chip for holding the fluid. The device and top of the package is then epoxied in (D) to protect the wire bonds and prevent fluid leakage, while leaving the well area open to fluid transfer.



3-aminopropyldimethlyethoxysilane (APDMS)



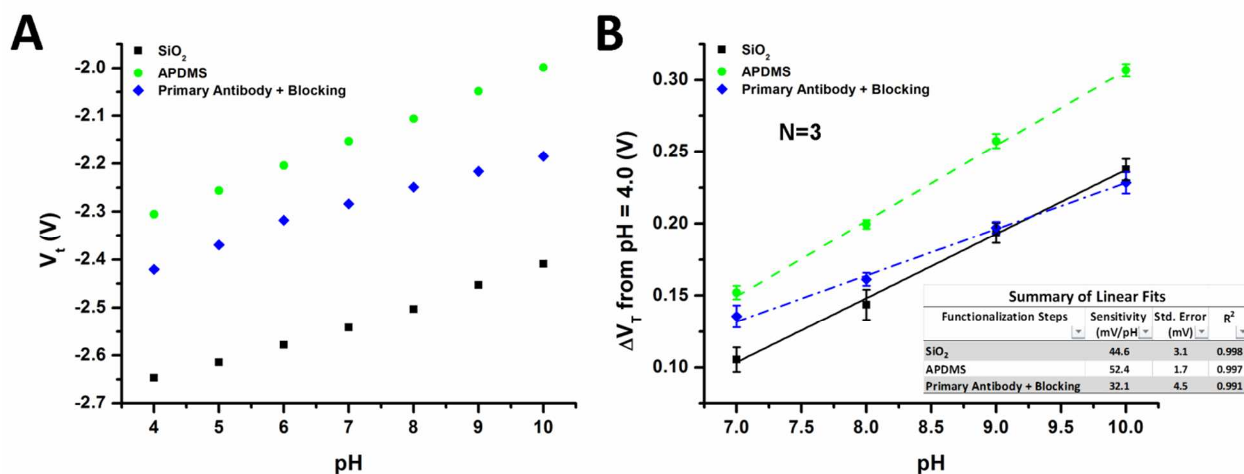
Disuccinimidyl carbonate (DSC)



Bis(succinimidyl) penta(ethylene glycol) (BS(PEG))

Glutaraldehyde

Supplementary Figure 2. Chemical structures of the monolayer and the different linking chemistries used in the functionalization protocols. The acronyms used in the manuscript are in brackets next to the chemical name.



Functionalization Steps	Sensitivity (mV/pH	Std. Error (mV)	R^2
SiO_2	44.6	3.1	0.998
APDMS	52.4	1.7	0.997
Primary Antibody + Blocking	32.1	4.5	0.991

Supplementary Figure 3. The threshold voltage (Vt) vs. the solution pH for different layers in the nanowire functionalization process is shown in (A). The change in threshold voltage (ΔVt) from pH 4.0 vs. the pH is in (B) with linear fits for each of these layers starting from pH 7.0. A table with the extracted parameters from the linear fits for pH sensitivity in (B, inset). Measurements were taken in 0.01x PBS, pH 7.4.

References

(1) Reddy, B.; Elibol, O. H.; Nair, P. R.; Dorvel, B. R.; Butler, F.; Ahsan, Z.; Bergstrom, D. E.; Alam, M. A., Bashir, R., *Anal. Chem.* 2011, *83*. 888-895, DOI: Doi 10.1021/Ac102566f.

(2) Dorvel, B.; Reddy, B.; Block, I.; Mathias, P.; Clare, S. E.; Cunningham, B.; Bergstrom, D. E., Bashir, R., *Adv. Funct. Mater.* 2010, *20*. 87-95, DOI: DOI 10.1002/adfm.200901688.