Supporting Information

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SI Text

Nanowire Synthesis. Au nanoclusters (Ted Pella Inc.) with 30-nm diameters were dispersed on the oxide surface of silicon/SiO_2 substrates (600 nm oxide) and placed in the central region of a quartz tube chemical vapor deposition reactor system. Uniform 30-nm p-type silicon nanowires were synthesized using reported methods (1). In a typical synthesis, the total pressure was 40 torr, and the flow rates of SiH_4, diborane (B_2H_6, 100 ppm in H_2), and hydrogen (H_2, semiconductor grade) were 2, 2.5, and 60 standard cubic centimeters per minute (SCCM), respectively. The silicon-boron feed-in ratio was 4,000:1, and the total nanowire growth time was 30 min.

Fabrication of 3D Macroporous Nanoelectronic Networks. Key steps used in the fabrication of the 3D macroporous nanowire nanoelectronic networks were as follows (*SI Text*): (*i*) Lithography and thermal deposition were used to pattern a 100-nm nickel metal layer, where the nickel served as the final relief layer for the 2D free-standing macroporous nanowire nanoelectronic networks. (*ii*) A 300- to 500-nm layer of SU-8 photoresist (2000.5; MicroChem Corp.) was deposited over the entire chip, followed by prebaking at 65 °C and 95 °C for 2 and 4 min, respectively, then (*iii*) the synthesized nanowires were directly printed from growth wafer over the SU-8 layer by the contact printing. (*iv*) Lithography (photolithography or electron beam lithography) was used to define regular patterns on the SU-8. After postbaking (65 °C and 95 °C for 2 and 4 min, respectively), SU-8 developer (MicroChem Corp.) was used to develop the SU-8 pattern. Those areas exposed to UV light or electron beam became dissolvable to SU-8 developer, and other areas were dissolved by SU-8 developer. Those nanowires on the nonexposed area will be removed by further washing away in isopropanol solution (30 s) twice, leaving those selected nanowires on the regular pattern SU-8 structure. The SU-8 patterns were cured at 180 °C for 20 min. (*v*) A 300- to 500-nm layer of SU-8 photoresist was deposited over the entire chip followed by prebaking at 65 °C and 95 °C for 2 and 4 min, respectively. Then lithography was used to pattern the bottom SU-8 layer for passivating and supporting the whole device structure. The structure was postbaked, developed, and cured by the same procedure as described above. (*vi*) Lithography and thermal deposition were used to define and deposit the metal contact to address each nanowire device and form interconnections to the input/output pads for the array. For the mesh device, in which the metal is nonstressed, symmetrical Cr/Pd/Cr (1.5/50–80/1.5 nm) metal was sequentially deposited followed by metal liftoff in acetone. For the self-organized networks, in which the metal is stressed, nonsymmetrical Cr/Pd/Cr (1.5/50–80/50–80 nm) metal was sequentially deposited followed by metal liftoff in acetone. (*vii*) A 300- to 500-nm layer of SU-8 photoresist was deposited over the entire chip, followed by prebaking at 65 °C and 95 °C for 2 and 4 min, respectively. Then lithography was used to pattern the top SU-8 layer for passivating the whole device structure. The structure was postbaked, developed, and cured by the same procedure as described above. (*viii*) The 2D macroporous nanowire nanoelectronic networks were released from the substrate by etching of the nickel layer (Nickel Etchant TFB; Transene Company Inc.) for 60–120 min at 25 °C. (*ix*) The 3D macroporous nanowire nanoelectronic networks were dried by a critical point dryer (Autosamdri 815 Series A; Tousimis) and stored in the dry state before use.

Characterization of Macroporous Nanoelectronic Networks. SEM (Zeiss Ultra55/Supra55VP field-emission SEMs) was used to characterize the macroporous nanoelectronic networks. Bright-field and dark-field optical micrographs of samples were acquired on an Olympus FSX100 system using FSX-BSW software (version 02.02). Fluorescence images of the 3D macroporous nanoelectronic networks were obtained by doping the SU-8 resist with rhodamine 6G (Sigma-Aldrich) at a concentration less than 1 μg/mL before deposition and patterning. ImageJ (version 1.45i, http://imagej.nih.gov/ij/) was used for 3D reconstruction and analysis of the confocal and epi-fluorescence images. Bending stiffness of the SU-8/metal/SU-8 ribbon was measured using an Asylum MFP-3D atomic force microscope (AFM) system with a calibrated AFM tip.

Mechanical Properties. The 3D macroporous nanoelectronic networks consist of single-layer polymer (SU-8) structural and three-layer ribbon (SU-8/metal/SU-8) interconnect elements. The effective bending stiffness per unit width of the 3D macroporous nanoelectronic networks can be estimated (2) by Eq. **S1**:

$$\overline{D} = \alpha_s D_s + \alpha_m D_m, \qquad [\textbf{S1}]$$

where α_s and α_m are the area fraction of the single-layer polymer and three-layer interconnect ribbons in the networks. $D_s = E_s h^3/12$ is the bending stiffness per unit width of the single-layer polymer, where $E_s = 2$ GPa and h are the modulus and thickness of the SU-8. For a SU-8 ribbon with 500-nm thickness, D_s is 0.02nN/m. D_m is the bending stiffness per unit width of a three-layer structure, which includes 500-nm lower and upper SU-8 layers and 100- to 130-nm metal layer, and was measured experimentally as described below and shown in Fig. S2.

Free-Standing Three-Layer Interconnect Ribbon Fabrication and Mechanical Testing. An Ni sacrificial layer was defined on a SiO_2/Si substrate (600 nm SiO_2, n-type silicon 0.005 V/cm; Nova Electronic Materials) by electron beam lithography (EBL) and thermal deposition. SU-8/metal/SU-8 elements with 100-μm-long and 5-μm-wide segments over the Ni layer, and wider segments directly on substrate, were defined by EBL using the same approach described in *Materials and Methods*. In brief, a 500-nm-thick SU-8 layer was deposited by spin coating and defined by EBL to serve as the bottom SU-8 layer. Then EBL, thermal deposition, and liftoff were used to define an asymmetrical metal layer consisting of a 3-μm-wide Cr/Pd/Cr (1.5/80/50 nm) ribbon centered on the bottom SU-8 element. Last, the top 500-nm-thick SU-8 layer of the SU-8/metal/SU-8 elements were defined, and then the Ni sacrificial layer was removed by Ni etchant, where the final drying step was carried out by critical point drying (Autosamdri 815 Series A; Tousimis). A schematic and an optical image of the resulting sample element are shown in Fig. S2 *A* and *B*, respectively. An AFM (MFP 3D; Asylum Corp.) was used to measure force vs. displacement curves for the SU-8/metal/SU-8 elements (Fig. S2*A*). The tip of the AFM was placed at the free end of the ribbon element, and then the applied force and displacement were recorded while the AFM tip was translated down (loading) and then up (unloading), with typical data shown in Fig. S2*C*. The spring constant of the AFM cantilever/tip assemblies used in the measurements were calibrated by measuring the thermal vibration spectrum (3).

Bending Stiffness Analysis. Due to the residual stress, The SU-8/metal/SU-8 elements bend upward from the substrate (due to

internal stress of the asymmetric metal layers) with a constant curvature, K_0, and projected length, l, where l_0 is the free length defined by fabrication. We use the curvilinear coordinate s to describe the distance along the curved ribbon from the fixed end, and the coordinate x to describe the projection position of each material point of the ribbon (Fig. S3A). For a specific material point with distance s, the projection position x can be calculated as $x = \int \cos\psi \, ds$, where $\psi = K_0 s$ is the angle between the tangential direction of the curvilinear coordinate s and the horizontal direction (Fig. S3B). Integration yields $x = \sin(K_0 s)/K_0$ and when $x = l$ and $s = l_0$, $K_0 = 0.0128 \, \mu m^{-1}$ for typical experimental parameters $l_0 = 100 \, \mu m$ and $l = 75 \, \mu m$.

Because the element is deflected a distance d by the AFM tip with a force F, each material point is rotated by an angle, φ (Fig. S3B), where the anticlockwise direction is defined as positive. Assuming a linear constitutive relation between the moment M and curvature change $d\varphi/ds$ (4) yields

$$\frac{d\varphi}{ds} = \frac{M}{wD_m}, \qquad \textbf{[S2]}$$

where M is the moment as a function of position, x (Fig. S3), and w is the width.

$$M(x) = -F(l - x) \qquad \textbf{[S3]}$$

Solving for the bending stiffness, D_m, with the assumption that φ is small so that $\sin\varphi \approx \varphi$ yields

$$D_m = \frac{F}{wd} \left(\frac{ll_0 \sin(K_0 l_0)}{K_0} + \frac{1}{K_0^2} \left(l\cos(K_0 l_0) - l + \frac{l_0}{2} \right) \right. $$
$$\left. + \frac{1}{K_0^3} \left(\frac{\sin(2K_0 l_0)}{4} - \sin(K_0 l_0) \right) \right). \qquad \textbf{[S4]}$$

The slope of a representative loading force-deflection curve yields $F/d = 12 \, nN/\mu m$ (Fig. S2C), and using Eq. **S4**, the calculated bending stiffness per width ($w = 5 \, \mu m$) is $D_m = 0.358 \, nN/m$. For typical 3D macroporous nanoelectronic networks, the area fraction for both types of elements (i.e., SU-8 and SU-8/metal/SU-8) can range from 1% to 10%, yielding values of the effective bending stiffness from 0.0038 to 0.0378 nN/m.

Three-Dimensional Macroporous Photodetectors and Device Localization. Confocal laser scanning microscopy (FluoView FV1000; Olympus America Inc.) was used to characterize the 3D macroporous nanoelectronic network. Conventional 405-nm and 473-nm wavelength lasers were used, with 405 nm to produce photocurrents in the nanowire transistor devices, and 473 nm for fluorescence imaging. The SU-8 structure was doped with rhodamine 6G for fluorescence imaging. The macroporous nanoelectronic network was immersed into deionized (DI) water; individual devices were biased with 100 mV; and 40× or 100× water-immersion objectives were used for imaging. The photocurrent signal was amplified (SIM 918; Stanford Research System) bandpass filtered (1–6,000 Hz, home-built system), and synchronized with laser scanning position using an analog signal input box (F10ANALOG; Olympus America Inc.). The conductance signal from the resulting images was read out by ImageJ, and the data were analyzed and fitted by OriginPro.

Three-Dimensional Macroporous Chemical Sensors. Agarose (Sigma) was dissolved into DI water, made as 0.5%, and heated up to 100 °C. The gel was drop-cast onto the device and cooled to room temperature. DAPI (Sigma) was used to dope the gel for the confocal 3D reconstructed imaging. A microfluidic polydimethylsiloxane (PDMS) fluidic chamber with input/output tubing and Ag/AgCl electrodes was sealed with the silicon substrate and the device or device/gel hybrid using silicone elastomer glue (Kwik-Sil; World Precision Instruments, Inc.). Fresh medium was delivered to the device region through both inner and outer tubing. The solution pH was varied stepwise inside the channel by flowing (20 mL/h) 1× phosphate buffered solutions with fixed pH values from pH 6 to 8. The recorded device signals were filtered with a bandpass filter of 0–300 Hz.

Three-Dimensional Macroporous Nanoelectronic/Elastomer Strain Sensors. A freestanding 2D macroporous nanoelectronic network was suspended in water and placed on a thin (200–500 μm) piece of cured silicone elastomer sheet (Sylgard 184; Dow Corning). The hybrid macroporous nanowire network/silicone elastomer was rolled into a cylinder, infiltrated with uncured silicone elastomer under vacuum, and cured at 70 °C for 4 h. The resulting hybrid nanoelectronic/elastomer cylinders had volumes of ~300 mm³ with volume ratio of device to elastomer of <0.1%. The structure of the macroporous electronics/elastomer hybrid was determined using a HMXST X-ray micro-CT system with a standard horizontal imaging axis cabinet (HMXST225; Nikon Metrology, Inc.). In a typical imaging experiment, the acceleration voltage was 60–70 kV, the electron beam current was 130–150 mA, and no filter was used. BGStudio MAX (version 2.0; Volume Graphics GmbH) was used for 3D reconstruction and analysis of the micro-CT images, which resolve the 3D metal interconnect structure and nanowire source/drain (S/D) contacts; the Si nanowires were not resolved in these images but were localized at the scale of the S/D contacts. The piezoelectric response to the strain of the nanowire devices was calibrated using a mechanical clamp device under tensile strain (Fig. S5), where the strain was calculated from the length change of the cylindrical hybrid structure. The bending strain field was determined in experiments where the cylindrical hybrid structure, with calibrated nanowire strain sensors, was subject to random bending deflections.

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Fig. S1. Interface to macroporous nanoelectronic network. Zoom-in of the region enclosed by the white dashed box in Fig. 2*D*. The white arrows highlight several wire bonds between the printed circuit board connector board and metal pads on the edge of the macroporous nanoelectronic network.

Fig. S2. Bending stiffness measurements. (*A*) Schematic illustrating the measurement of the bending stiffness of a representative SU-8/metal/SU-8 element in the macroporous nanoelectronic networks. Electron beam lithography is used to define substrate-fixed and substrate-free beams, where internal stress in the central metal layer causes the structure to bend up upon relief from the substrate (*SI Text*). The tip of the AFM is placed at the free end of the ribbon, and then translated vertically downward (loading) and upward (unloading) to yield the force-displacement curves. In the scheme: w, the width of the ribbon; l_0, the length of the ribbon; l, the projected length of the ribbon; and d, the displacement of the AFM tip. (*B*) Optical micrograph of the fabricated structural element, where the substrate-fixed portion is highlighted by the red dashed rectangle, and the free beam is in the upper portion of the image with a width of 5 μm and a length of 100 μm. (*C*) A typical force-displacement curve with F/d for loading and unloading of 12 and 10.5 nN/μm, respectively. Similar deviation between the loading and unloading has been attributed to inelastic deformation (1, 2); hence, we use the larger loading value in calculations to provide an upper limit.

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Fig. S3. Schematics for calculations. (*A*) A schematic of the position of the substrate-free beam before (black) and after (red) applying a calibrated force, F, and vertical displacement, d, at the end of the beam with the AFM. (*B*) The angle between the tangential direction of a material point on the beam and the horizontal direction, ψ, of the ribbon before (black) and after displacement, $\psi + \varphi$, (red). l_0, total length of the ribbon; l, projection of the ribbon.

Fig. S4. Localization of 3D macroporous nanoelectronic devices. The 3D macroporous nanoelectronic FET devices exhibit photoconductivity (1) that was used to determine spatial positions using a confocal microscope equipped with an analog signal input box (*Materials and Methods*). (*A*) Schematic of photocurrent detection and correlation with confocal microscopy laser spot scanning position. A 405-nm laser wavelength, 100× water-immersion lens, and 0.1-mV source/drain device bias-voltage were used in the experiments. (*B*) High-resolution (1 nm per pixel) photocurrent image (*I*) from a single nanowire device (2-μm channel length between upper/lower metal contacts) recorded scanning in *xy* plane. The red dashed line indicates the direction perpendicular to the nanowire axis. The black dashed lines indicate the boundaries of metal contacts. (*II*) Photocurrent measured along the red dashed line in *I*. Experimental data are fit with a Gaussian distribution (red solid curve). (*C*) Distribution of the center point positions determined from 20 independent scans in the region indicated in Fig. 3 *B, II* and about the single scan line (red dashed line) shown in Fig. 3 *B, I*.

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Fig. S5. Calibration of the 3D macroporous nanoelectronic strain sensors. (*A*) Conductance change vs. time as a 10% tensile strain was applied to hybrid 3D macroporous nanoelectronic networks/PDMS cylindrical sample. The downward- and upward-pointing arrows denote the times when the strain was applied and released, respectively. The direction of strain on the cylindrical hybrid sample and projected position of the macroporous nanoelectronic networks are indicated in the optical micrograph (*Right*). The conductance changes of 11 measured nanowire devices (labeled arbitrarily in terms of increasing sensitivity) were recorded and used for the conductance change per strain calibration. (*B*) Strain sensitivity calibration of the nanowire devices is plotted in 3D. The data points are color-coded by the sensitivity of the devices (*A*).