Biodegradable porous silicon barcode nanowires with defined geometry

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Abstract

Silicon nanowires are of proven importance in diverse fields such as energy production and storage, flexible electronics, and biomedicine due to the unique characteristics emerging from their one-dimensional semiconducting nature and their mechanical properties. Here we report the synthesis of biodegradable porous silicon barcode nanowires by metal assisted electroless etch of single crystal silicon with resistivity ranging from 0.0008 Ω-cm to 10 Ω-cm. We define the geometry of the barcode nanowires by nanolithography and we characterize their multicolor reflectance and photoluminescence. We develop phase diagrams for the different nanostructures obtained as a function of metal catalyst, H₂O₂ concentration, ethanol concentration and silicon resistivity, and propose a mechanism that explains these observations. We demonstrate that these nanowires are biodegradable, and their degradation time can be modulated by surface treatments.

Keywords

Nanowires; Porous Materials; Semiconductors; Photonics; Electrochemistry

1. Introduction

The quantum sponge structure of Porous Silicon (pSi) has attracted interest for potential applications in very diverse fields due to the combination of quantum confinement effects, permeability to molecules and nanoparticles, large internal surface area for

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Supporting Information is available online from Wiley InterScience or from the author.
molecular interactions. These features, combined with pSi biodegradability and biocompatibility have stimulated research for biomedical applications such as implantable devices, drug delivery systems and tissue engineering scaffolds. The tunable photoluminescence of pSi in the infrared to visible region holds promise for the development of biocompatible nonbleaching fluorophores for in-vitro and in-vivo biolableing.

Furthermore Silicon Nanowires (SiNWs), owing to their one-dimensional structure and mechanical properties, are under intensive study for photovoltaics, energy storage, nanoscale and flexible electronics, and photonic devices. SiNW hierarchical superstructures synthesized by chemical vapor deposition are being studied for the realization of diodes and transistors. SiNWs have been exploited to study the behavior of motor proteins and cell adhesion mechanisms. Several biosensors based on SiNWs have been developed for glucose monitoring, multiplexed protein detection, label-free DNA detection, single-virus detection.

Metal-assisted etch has emerged as a method to obtain either porous silicon or silicon nanowires in an oxidant HF solution. Recently the formation of porous silicon nanowires (pNWs) from low resistivity p-type silicon by electroless etch in a solution of HF, H$_2$O$_2$ and AgNO$_3$, and pNWs from low resistivity n-type silicon by electroless etch in a solution of HF, H$_2$O$_2$ following deposition of Ag nanoparticles in a solution of HF and AgNO$_3$ were reported. pNWs couple the nanowire one-dimensional structure to the unique characteristics of porous silicon, showing promise for the realization of flexible, biodegradable electronic and photonic biomedical devices with high sensitivity to the surrounding environment. In this study we show the synthesis of pNWs regardless of silicon resistivity. We employ metal assisted electroless etch to synthesize porous silicon barcode nanowires (nanobarcodes) with geometry defined by lithography. The different porosity of each nanobarcode segment determines its specific reflection and emission spectra, and yields multicolor nanobarcodes. We enhance the segment-specific fluorescence of nanobarcodes by differential loading of two sizes of quantum-dots (Q-dots). We present phase diagrams that describe the effect of metal catalyst, composition of the etching solution, Si doping type and resistivity on the resulting silicon nanostructures: solid nanowires, porous nanowires, porous nanowires on porous silicon film, porous silicon films and polished surfaces. We furthermore demonstrate that porous silicon nanowires dissolve in simulated physiological conditions, and their dissolution rate can be controlled by surface functionalization.

## 2. Results and Discussion

### 2.1. Porous silicon nanobarcodes

We synthesize nanobarcodes by periodically varying the porosity along the major axis of the porous silicon nanowires during their formation(Figure 1). The color and photoluminescence of each segment is determined by its porosity. We modulate the porosity by periodically adjusting the hydrogen peroxide concentration in a 2.9 M HF aqueous solution; relatively higher concentration of H$_2$O$_2$ results in segment with higher porosity and larger pores as the N$_2$ absorption/desorption isotherms indicate. P-type silicon wafers with resistivity <0.005 Ω·cm etched in 0.1 M H$_2$O$_2$ result in 47% porosity and 6.1 nm peak pore size as measured according to the Brunauer-Emmett-Teller and Barrett-Joyner-Halenda methods respectively, while the same substrates etched in 0.2 M H$_2$O$_2$ result in 66% porosity and 11.4 nm pores (Supplementary Figure 1). Scanning Electron Microscope (SEM) analysis shows that the porosity transition between adjacent segments occurs within a few nanometers, indicating a prompt response to the change in H$_2$O$_2$ concentration (Figure 1a, Supplementary Figure 2).
The nanobarcodes exhibit sharply defined, spatially varying colors under (3200K halogen lamp) white light as a result of the different reflection spectrum associated with each segment(Figure 1 d). The porosity of each segment determines its refraction index, its optical thickness and thus the resulting color. Under the incidence angle of the optical microscope, high porosity segments show a red color, while the low porosity segments show a green color. The multicolor photoluminescence of the synthesized nanobarcodes is measured by photoluminescence spectrometry. We analyze the photoluminescence of low-porosity nanowires (synthesized in solution containing 0.05 \( \text{M} \) \( \text{H}_2\text{O}_2 \)), high porosity nanowires (0.2 \( \text{M} \) \( \text{H}_2\text{O}_2 \)) and bicolor nanobarcodes (six alternated low-, high-porosity links) suspended in isopropyl alcohol. The low porosity nanowires exhibit a broad emission peak centered at 450 nm while high porosity nanowires show a similar peak centered at 540 nm (Figure 1 c). The photoluminescence of the nanobarcodes is the result of the superposition of spatially distinct contribution from low and high porosity segments; in fact their spectrum matches the superposition of the individual spectrum of high porosity and low porosity nanowires (Figure 1 c). Furthermore confocal microscopy analysis of bicolor nanobarcodes under 458 nm laser shows alternating dark and bright areas that match respectively the high and low porosity chain links (Figure 1 b).

Porous silicon photoluminescence quantum efficiency is known to be low,[41] and might not be sufficient for applications in environments with elevated background noise. Also the absorption band of the nanobarcodes may fall in the UV range (Supplementary Figure 2), limiting their practical application. We obtain highly efficient multicolor fluorescent nanobarcodes by differential loading of Bare CdSe red (6.6 nm diameter, 633nm emission) and yellow (3.3nm diameter, 560nm emission) Q-dots into the pores of different segment of the same nanobarcode(Figure 1 e). The spectrum of loaded nanobarcodes shows two sharp peaks centered at the emission wavelength associated with the Q-dots (Figure 1 f). Three channel confocal fluorescence microscopy indicates that the larger red Q-dots only load into the large pore, high porosity segments, while the smaller yellow Q-dots load almost exclusively into the small pore, low porosity segments resulting in a high efficiency fluorescent two-color nanobarcode (Figure 1 e) and showing the ability to harvest nanoparticles from solution based on size selectivity. While the absence of 6.6nm Q-dots in the small pores is explained in terms of size exclusion, the preferential loading of 3.3nm Q-dots within smaller pores could be due to more conformal surface interaction between curvature-matched pore and Q-dot surfaces that minimizes the surface energy. Meanwhile clustering of the 3.3nm Q-dots within large pores to minimize surface energy is forbidden in our system due to the size of large pores (11.4nm). Therefore smaller Q-dots are less populated in the barcode segments with larger pores size.

### 2.2. Defining the geometry of nanobarcodes by nanolithography

While the simple deposition of metal from HF-metal salt solution allows for the facile synthesis of porous silicon nanowires and nanobarcodes, it does not grant control over the shape, size and array density of the nanowires. Yet tightly controlled geometry of porous silicon nanostructures is desired for practical applications such as integrated optical, photonic and sensing systems. Nanolithography, along with metal-assisted etch has been applied in the synthesis of solid silicon nanopillars of defined geometry and density.[42] Nanosphere lithography provides a facile and inexpensive method to control the diameter of nanopillars while photolithography grants control over position, density, shape, and size of the nanoporous structures (Figure 2). We synthesize 2 \( \mu \text{m} \times 2 \mu \text{m} \times 600\text{nm} \) nanoplatelets with 600nm spacing over an entire 100nm wafer by contact photolithography(Figure 2 b, d). We form of 120nm \times 5\mu m porous silicon nanopillars in organized layers extending over several microns by nanosphere lithography with 160nm diameter polystyrene beads(Figure 2 b, d).
2.3. Biodegradation of porous silicon nanowires

To probe the adequacy of porous silicon nanowires and nanobarcodes as building blocks for biodegradable sensors, we investigate the pNWs behavior in simulated physiological conditions. Porous nanowires are placed in phosphate buffered saline for up to 96 hours and analyzed by scanning electron microscopy (Figure 3). We observe that as synthesized <0.005 Ω-cm pNWs degrade completely in 24h, while the same pNWs that undergo oxygen plasma oxidation degrade in 72 hours, indicating that surface treatment influences the degradation rate. Conversely 0.01-0.02 Ω-cm solid nanowires do not show obvious degradation over a 96 hours experimental period. The pNW display a progressive thickness reduction without exhibiting significant shortening and become more flexible over time, as evidenced by spontaneous bending (Figure 3, Porous NW: 48h). We observe that pore size increases with time in accord with degradation of the material. As-synthesized pNWs more than double their pore size within 16h whereas oxidized nanowires do not exhibit appreciable pore size increase until 48h.

2.4. Formation of silicon nanostructures

To attain control over the photonic and mechanical properties of the nanobarcodes it is necessary to fully understand how the etch determines the resulting silicon nanostructures as well as the details of their formation. We observe that metal assisted etch of silicon results in nanostructures with different morphologies depending on few key process parameters. Figure 4 shows SEM micrographs of the five distinguishable morphologies resulting from the Au and Ag assisted etch of silicon: solid nanowires (Figure 4 a, sNWs), porous nanowires (Figure 4 b, pNW), porous nanowires on the top of porous silicon film (Figure c,d, pNW+PS), porous silicon films (Figure 4 e, PS) and polished silicon surfaces (Figure 4 f). The key parameters controlling the resulting morphology are silicon resistivity, H\textsubscript{2}O\textsubscript{2} concentration, metal employed, and concentration of surfactant (ethanol), while HF concentration only influences the etch rate. The combined effects of these factors are illustrated in a series of phase diagrams (Figure 5). The phase diagrams indicate a well-defined, smooth morphological transition sequence from sNWs to pNWs to pNW+PS to PS (when present) to polished surfaces. Substrates of low resistivity transition to every successive morphological state at lower concentrations of H\textsubscript{2}O\textsubscript{2} than their high resistivity counterparts. Substrates <0.005 Ω-cm form sNW only at H\textsubscript{2}O\textsubscript{2} concentrations lower than 0.03M while 0.0008-0.001 Ω-cm substrates do not form sNW in any condition examined, but form very flexible thin spaghetti-like pNWs on porous silicon at low H\textsubscript{2}O\textsubscript{2} concentrations (Figure 4 d). The sidewalls of these spaghetti-like pNWs are an extension of walls of the underlying porous layer. These same nanostructures can be obtained under comparable conditions employing n-type silicon (not shown), indicating that doping type does not play a significant role in determining the type of nanostructures that can be obtained.

With all other parameters fixed, decreasing the resistivity of silicon induces a smooth transition in the morphology phase diagram from sNWs towards polished surfaces (Figure 5 a, b, e). We observe the same smooth sNWs to polished surface transition when increasing the concentration of H\textsubscript{2}O\textsubscript{2} in the etch solution while all other parameters are kept fixed (Figure 5 a,b). With increasing H\textsubscript{2}O\textsubscript{2} the cross section of the porous nanowires reduces in diameter until it matches the wall thickness of the underlying porous silicon and further increase in the H\textsubscript{2}O\textsubscript{2} concentration induces the disappearance of the SiNWs resulting in either PS or polished surfaces. H\textsubscript{2}O\textsubscript{2} concentration and silicon conductivity also positively correlates with average pore size and porosity of the nanowires (Supplementary Figure 1).
The SEM analysis indicates that thinner nanowires and nanowires with larger pores are more prone to bend spontaneously, suggesting a lower flexural modulus. The noble metal catalyst also affects the morphological transition boundaries. Au assisted etch forms porous structures for substrates with resistivity as high as 1-10 Ω-cm, while Ag only forms porous structures up to 0.1-0.2 Ω-cm. The phase space region for the formation of pNW is wider for Au than for Ag, and polishing of the surface is less likely to occur for Au and occurs at higher H₂O₂ concentrations than with Ag. Upon addition of ethanol, meant to improve the wetting of the water-based solution on the silicon surface, the smooth sequential transition from sNW to polished surface re-appears, characterized by the presence of a PS morphological phase in between the pNW+PS and the polishing phases (Figure 5 e).

The SiNW etch rate is positively correlated with resistivity from 0.0008-0.001 Ω-cm to 1-10 Ω-cm (Figure 5 c). Etch rate is positively correlated with H₂O₂ concentration from 0.05 m to 0.8 m (Figure 5 d). Increasing the concentration of ethanol instead decreases the SiNW etch rate (Figure 5 f). The absence of pNWs and the formation of PS for substrates with resistivity lower than 0.01-0.02 Ω-cm at elevated ethanol concentration is thus explained by the combined etch rate suppression of these two parameters. The etch rates for Au and Ag are comparable in all instances.

We observe a remarkable difference in the porous structure of pNWs and pNW+PS (Figure 6): pNWs pores grow from the sidewall towards the major axis of the nanowire (Figure 6 a), while pNW+PS pores grow parallel to the major axis, along the SiNW etch direction (Figure 6 b) and extend as continuous structures from the pNW into the underlying PS layer. The evolution of the porous structure orthogonal to the pNW wall is illustrated in enlarged nanowire patterns (5μm circular array, Supplementary Figure 4) and indicates that the difference in porous structure between pNWs and pNW+PS is the result of a different formation mechanism. A porosification rate slower than the SiNW etch rate characterizes solid or partially porosified SiNWs and results in the porosification of the SiNW walls after they are exposed by the metal nanoparticle assisted etch (Figure 6 a, c). A porosification rate matching the SiNW etch rate characterizes pNWs (Figure 4 b); on the contrary, a porosification rate faster than the SiNW etch rate characterizes pNW+PS and results in the formation of a porous silicon layer that is then partially etched into SiNWs by the action of the metal nanoparticles (Figure 6 b, d).

A model recently proposed hypothesizes that the formation of nanowires during metal assisted etch is catalyzed by the primary deposited metal nanoparticles (NPs) while the porosification is catalyzed by secondary NPs resulting from aggregation of ions shed by the primary NPs.[40] Our results do not support this model and suggest an alternative whereby SiNW formation is catalyzed by the primary NPs while the porosification is catalyzed by the metal ions in solution without formation of secondary NPs. Support for this hypothesis is found in our observation that metal NPs are not detected within the pores of the SiNW or at the bottom of the porous layer by SEM (Figures 4, 6), TEM (Supplementary Figure 5) or STEM/EDX analysis. Furthermore all detectable NPs in pNW+PS accumulate at the interface between the nanowires and the porous layer and thus cannot be the catalyst for the formation of the PS layer (Figure 4 c-e, Figure 6 b). We also observe formation of porous silicon layers on blank wafers when placed in the same solution as the metal deposited ones either during the metal assisted etch or after completion of an etch (without any detectable metal NP on the blank wafers), but no porosification occurs on blank wafers in electrolyte solution alone (Supplementary Figure 7). This phenomenon indicates a possible route for the porosification of silicon nanowires produced through other means.
Within the framework of this model the different morphologies obtained are explained in terms of the relative catalytic activity of the ions \( C_i \) that determine the porosification rate and the catalytic activity of the nanoparticles \( C_n \) that determine the SiNW etch rate. \( C_i \) and \( C_n \) are operationally defined in terms of the porosification rate \( v_p \) and SiNW etch rate \( v_e \) respectively:

\[
C_i = v_p = \frac{\Delta x_p}{\Delta t_p}
\]

\[
C_n = v_e = \frac{\Delta x_e}{\Delta t_e}
\]

Where \( \Delta x_p \) is the thickness of the porous layer formed during a porosification time \( \Delta t_p \) and \( \Delta x_e \) is the length of the nanowires obtained during an etch time \( \Delta t_e \) (Figure 6 c,d). We then define the catalytic activity ratio \( C_0 \) as

\[
C_0 = \frac{C_i}{C_n} = \frac{v_p}{v_e} = \frac{\Delta x_p}{\Delta x_e}
\]

Since it is always possible to choose \( \Delta t_p = \Delta t_e \).

Our experiments show that increasing the concentration of ethanol reduces \( v_e \) indicating a reduction in \( C_n \) (Figure 5 f) while it does not appear to dramatically affect \( C_i \). The net effect of reducing \( v_e \) results in an increase in \( C_0 \) and explains the morphological transitions associated with increasing ethanol concentrations. Ion concentration in solution contributes to determine \( C_i \) and thus the porosification rate. Hydrogen peroxide plays a fundamental role in maintaining the noble metal ion pool during the etch process, and \( H_2O_2 \) local concentration determines the dynamics of ion recycling.[43] The Si etch reaction involving Ag

\[
4Ag^+ + Si^0 + 6F^- \rightarrow 4Ag^0 + [SiF_6]^{2-}
\]

Reduces metal ions depleting the pool, increasing the concentration of neutral species in solution and potentially inducing their precipitation and nucleation into secondary nanoparticles. Hydrogen peroxide in acidic conditions replenishes the ion pool through oxidation of the solvated neutral species:

\[
2Ag^0 + H_2O_2 + 2H^+ \rightarrow 2Ag^+ + 2H_2O
\]

At sufficiently high \( H_2O_2 \) concentration, this oxidation process prevents coalescence of neutral species inhibiting formation of secondary nanoparticles and sustaining the pool of ions in solution. In these conditions ions initially shed from the nanoparticle are constantly re-oxidized and can catalyze multiple sequential etch reactions, leading to substrate porosification. Nonetheless as the distance from the metal nanoparticle increases, the ion concentration diminishes, accompanied by a reduction in the porosification activity, allowing formation of segments with different porosity. Conversely at lower \( H_2O_2 \) concentrations, less species are oxidized and shed and most of the solvated ions react only...
few times, in close proximity to the primary nanoparticle, whereupon they become neutralized and can be readily re-incorporated into the original particle, contributing negligibly to substrate porosification and leading to the formation of solid nanowires.

In this hypothesis sNWs are the result of $C_0 \ll 1$ where the nanoparticles etch the SiNW quickly, while the ions porosify the SiNW slowly resulting at most in roughening of the SiNW. Transition to pNWs occurs when $C_0 \geq 1$ and the walls of the SiNWs become porosified readily after exposure to the electrolyte (Figure 6c). Transition to pNWs+PS occurred when $C_0 > 1$ and the silicon is porosified before the SiNWs are formed (Figure 6d). The formation of PS layers occurs when $C_0 \gg 1$, due to the almost complete inhibition of nanoparticles activity ($C_0 \approx 0$) at low resistivity and high ethanol concentration. Finally the transition to polished surfaces is due to the combined increase of $C_i$ and the increase in porosity and pore size associated with higher concentrations of $\text{H}_2\text{O}_2$.

3. Conclusions

We have demonstrated the synthesis of silicon nanobarcodes with multiple segments of different porosities by tuning the concentration of hydrogen peroxide during metal assisted electroless etch. We investigated the optical properties of the nanobarcodes observing segment specific reflection and emission spectra. We demonstrated control over size, shape and array density of the nanostructures by means of nanoscale lithography, and tuned their morphology (solid nanowires, porous nanowires, porous nanowires on porous layers, porous silicon layers or polished surfaces) by controlling a few key etch parameters (silicon resistivity, $\text{H}_2\text{O}_2$ concentration, ethanol concentration). We have developed phase diagrams describing the effect of key parameters on the nanostructures, and proposed a mechanism that explains our observations vis a vis alternative explanations. We showed that porous nanowires are biodegradable in simulated physiological conditions, and that the degradation rate can be controlled by surface functionalization.

We anticipate that the facile, predictable and controllable synthesis process presented will accelerate the development and refinement of devices and nanostructures for a variety of applications. For example, the tunable porosity of silicon nanobarcodes can be exploited as an alternative to porous silicon electrodes for supercapacitors[45] or to improve the efficiency of silicon based photovoltaic cells.[46] The pNWs’ ease of synthesis, large surface area, biodegradability, mechanical, optoelectronic and photonic properties could be exploited in the development of short-term implantable bendable biosensors for high sensitivity detection. The characteristic size, the spatial control over the reflection and the photonic properties of the nanobarcodes can be exploited for simultaneous biolabeling[47] and detection via bright field and fluorescence microscopy. These features of the nanobarcodes may find future application in live and in-vivo imaging owing to their full biodegradability.

4. Experimental

Metal Deposition

Ag or Au nanoparticles from metal salt solutions were deposited by electroless deposition[39] on 4” P-type (100) 0.0008-0.001 Ω-cm (Unisill, Korea), <0.005 Ω-cm, 0.01-0.02 Ω-cm, 0.1-0.2 Ω-cm, and 1-10 Ω-cm (Silicon Quest, Santa Clara, CA, USA) silicon wafers. The substrates were cleaned and stripped of their native oxide by soaking in 2.9M HF solution. The substrates were then transferred to the deposition solution: 2.9M HF, 0.02M AgNO₃ (Sigma-Aldrich, St. Louis, MO, USA) in the dark for Ag deposition; and 2.9M HF, 0.002M HAuCl₄ (Sigma-Aldrich, St. Louis, MO, USA) for Au deposition. Metal deposition time was regulated (20s to 4 min) according to the substrate resistivity to achieve
a constant and uniform Au or Ag nanoparticle layer. The metal-deposited substrates were thoroughly rinsed with DI water and dried.

Metal-assisted Chemical Etching

Following metal catalyst deposition, the Si wafers were etched in a water solution of HF, H$_2$O$_2$ and ethanol. The effect of HF concentration was studied by etching Ag-deposited wafers for 5 min in aqueous solutions of 1.5 M, 2.9 M, 4.5 M or 5.8 M HF with 0.2 M H$_2$O$_2$. The H$_2$O$_2$-resistivity phase diagrams and etch rates were studied by etching the wafers deposited with Ag or Au for 5 min in 0.05 M, 0.1 M, 0.2 M, 0.4 M, 0.8 M, 2 M or 4 M H$_2$O$_2$ in 2.9 M HF. The ethanol-resistivity phase diagrams and etch rates were studied by etching Ag-deposited wafers for 5 min in 0 M, 1.7 M, 3.4 M, 6.9 M, 13.7 M ethanol in 2.9 M HF with 0.2 M H$_2$O$_2$. Following the etch process, the substrates were rinsed with excess water, dried and prepared for electron microscopy imaging.

Multi-color Silicon nanobarcodes

Nanobarcodes were obtained by Ag assisted etch of $<$0.005 Ω-cm p-type Si wafer at varying H$_2$O$_2$ concentration. Ag was deposited on the substrate as described in the metal deposition section. The two-step cycle consisted of 10 min etch in 0.05 M H$_2$O$_2$, 2.9 M HF, followed by 1 min etch in 0.2 M H$_2$O$_2$, 2.9 M HF. The cycle was repeated thrice to obtain bicolor, six link nanobarcodes. Nanosphere lithography combined with this method was used to fabricate multi-color nanopillars.

Photoluminescence

Two-color nanobarcode and porous nanowires (Ag assisted, 0.05 M and 0.2 M H$_2$O$_2$) were mechanically removed from their respective substrate and collected in isopropyl alcohol. The photoluminescence spectra were acquired using a fluorometer (Quanta Master C, Photon Technologies International, Birmingham, NJ, USA) from 4 ml samples in a quartz cuvette with a 360 nm excitation wavelength. Polystyrene beads in isopropyl alcohol were used as negative control. The photoluminescence images were acquired from samples sealed on a glass slide with a Leica TCS SP5 confocal microscope (Leica Microsystems, Bannockburn, IL, USA). Q-dot enhanced photoluminescence samples were prepared by loading 100 μl of 2 mg/ml yellow (3.3 nm diameter, 560 nm emitting wavelength, NN-Labs, Fayetteville, AR, USA) CdSe Q-dots in 20 μl of porous nanowires for 30 minutes, followed by 200 μl of 2 mg/ml red (6.6 nm diameter, 633 nm emitting wavelength, NN-Labs, Fayetteville, AR, USA) CdSe Q-dots for 30 minutes, and rinsed in hexane. The samples were spread and sealed on glass slides and analyzed with the Leica confocal microscope.

Patterned porous silicon nanowires

We employed established methods of nanosphere lithography to prepare porous silicon nanopillars[44]. A 10% aqueous sol of 160 nm polystyrene spheres (Thermo Fisher Scientific, Waltham, MA, USA) was diluted to 2% sol in 400:1 (v/v) methanol/ Triton1000 (Thermo Fisher Scientific, Waltham, MA, USA). 50 ml of the suspension was spun at 2500 rpm for 60 s on $<$0.005 Ω-cm p-type Si substrate to obtain a close-packed polystyrene sphere monolayer. The sphere size was reduced to 130 nm by O$_2$ plasma etch (1 min 20 s, 25 sccm O$_2$, 10 mTorr, 100 W RF, Oxford PlasmaLab 80, Oxford Instruments, Abingdon, UK). Alternatively, we used standard photolithography (Futurrex NR9-250P resist, Futurrex, Franklin, NJ, USA) with nanometric feature masks (HTA Photomask, San Jose, CA, USA) to obtain nanoribbons (400 nm × 2 μm patterns, 600 nm pitch) and widely spaced nanopillars (600 nm diameter pattern, 1400 nm pitch). A 20 nm thick Ag film was deposited on the substrate by thermal evaporation with the polystyrene spheres or the photolithographic pattern acting as a stencil mask. The spheres were subsequently removed from the substrate.

Adv Funct Mater. Author manuscript; available in PMC 2011 July 23.
by sonication in Toluene for 30 min. The substrate was etched in a 2.9M HF and 0.1M H₂O₂ aqueous solution for 5 minutes.

**Biodegradation**

Porous and solid SiNWs were synthesized respectively from Ag deposited <0.005 Ω-cm and 0.01-0.02 Ω-cm p-type wafers etched for 5 min in 0.1M H₂O₂, 2.9M HF. Following SiNW formation, the metal nanoparticles were removed by 30s silver etch (Type TFS, Transene, Danvers, MA, USA). The substrates were cleaved into 1cm² samples; half of the solid and porous SiNW samples were oxidized by 1min oxygen plasma (PX-250 Asher, March Plasma Systems, Concord, CA, USA). Each sample was placed in 50ml phosphate buffered saline (Thermo Fisher Scientific, Waltham, MA, USA) on a rocker plate operating at 20rpm for the entire duration of the experiment. Samples were collected at 0, 2, 4, 8, 16, 20, 24, 48, 72, and 96 hours, rinsed with excess DI water, dried and imaged with a Zeiss Neon40 FE-SEM (Carl Zeiss SMT, Peabody, MA, USA).

**Supplementary Material**

Refer to Web version on PubMed Central for supplementary material.

**Acknowledgments**

We acknowledge Donald Erm, Hayiu Huang and Jeffrey Schmulen for their invaluable technical support. We thank Louis Brousseau, Angela Bardo, Daniel Fine and Colin Hessel for valuable discussions and Alessandro Grattoni for the help in absorbance spectrum measurement. The nanowire synthesis, electron microscopy and reflection microscopy were performed in the Microelectronics Research Center at University of Texas (UT) Austin; photoluminescence analysis was performed at the Institute for Cellular and Molecular Biology-UT Austin; confocal microscopy was performed at the Institute of Molecular Medicine at UT-Health Science Center at Houston; N₂ absorption/desorption analysis was performed at Rice University (Shared Equipment Authority). We acknowledge support from the State of Texas’s Emerging Technology Fund, NASA (NNJ06HE06A), Department of Defense (W81XWH-07-2-0101, W911NF-09-1-0044, W81XWH-09-1-0212), National Institute of Health (R01CA128797, U54CA143837) and the Alliance for NanoHealth (ANH).

**References**


Figure 1.
Porous silicon nanobarcodes. (a) Scanning electron micrographs of <0.005 Ω-cm barcodes. The nanobarcodes were obtained by Ag assisted etch (0.05M H₂O₂ for 5 min followed by 0.2M H₂O₂ for 1 min, repeated three times) Left: lateral overview as synthesized nanobarcodes showing the alternation of high porosity and low porosity segments. Right: Close up view of the high-low porosity transition of a single nanobarcode (Scale bar is 100 nm). (b) Confocal microscopy images of porous SiNWs; from top to bottom: Bright field image of a <0.005 Ω-cm 0.1 M H₂O₂ porous SiNW; fluorescence image of the same nanowire at 500nm wavelength emission; Fluorescence image of a <0.005 Ω-cm 0.05 M/0.2 M H₂O₂ nanobarcode at 500nm wavelength; bright field image of the same nanobarcode. (c) Photoluminescence spectra of porous SiNW in isopropyl alcohol. The photoluminescence spectrum corresponding to the 0.05 M/0.2 M H₂O₂ nanobarcode agrees well with the spectrum resulting from the superposition of the 0.05 M H₂O₂ and the 0.2 M H₂O₂ spectra. Initial sample concentration is unknown thus spectra have been scaled (90% of original 0.05 M H₂O₂, 50% of original 0.2 M H₂O₂) to minimize the absolute value residuals between the nanobarcode and the superposition spectra. Polystyrene beads have been employed as negative control and used to subtract background. (d) Reflection Microscopy image of a 0.05 M/0.2 M H₂O₂ nanobarcode showing the different colors associated with each segment. High porosity: red, low porosity: green. (e) Confocal microscopy images of a Q-dots loaded 0.05 M/0.2 M H₂O₂ nanobarcode under 458 nm excitation. From top to bottom: Fluorescent signal at 560nm, Fluorescent signal at 633nm, bright field signal, superposition. (f) Photoluminescence spectrum of Q-dots loaded 0.05 M/0.2 M H₂O₂ nanobarcode showing Q-dots associated peaks at 560nm and 633nm.
Figure 2.
Nanopatterned porous silicon structures. Scanning electron micrographs of: (a) 20 nm thick electron-beam evaporated Ag film on silicon deposited through a 130 nm diameter, 30 nm pitch stencil mask, obtained by nanosphere lithography with 160 nm polystyrene beads. (b) 16 nm thick electron-beam evaporated Ag film on silicon deposited through 400 nm × 2000 nm, 600 nm pitch stencil mask, obtained by photolithography (c) 130 nm diameter porous silicon nanopillars obtained by metal assisted etch of the pattern shown in (a) in 0.05 M H₂O₂ for 20 min. (d) 400 nm × 2000 nm × 2000 nm porous silicon platelets obtained by metal assisted etch of the pattern shown in (b) in 0.1 M H₂O₂ for 5 min.
Figure 3.
Degradation of porous silicon nanowires. Top: Scanning electron micrographs of non-oxidized 0.01-0.02 Ω-cm solid silicon nanowires following immersion in phosphate buffered saline; no degradation is observed within a 96h timeframe. Bottom: Scanning electron micrographs of oxidized <0.005 Ω-cm porous silicon nanowires following immersion in phosphate buffered saline; the porous nanowires show significant signs of degradation with loss of flexural modulus at 48h without exhibiting shortening; the wires are completely degraded after 72h immersion.
Figure 4.
Silicon nanostructure morphology is a function of the etch parameters. Cross sectional Scanning electron micrographs of the different silicon nanostructure morphologies obtained by metal assisted etch. The inset is a magnification of the sample shown in the cross section focusing on the structure of a single nanowire. (a) Solid silicon nanowires: 1-10 Ω-cm, Ag, 0.1 M H₂O₂, 15 min. (b) Porous silicon nanowires: <0.005 Ω-cm, Ag, 0.1 M H₂O₂, 15 min. (c) Thick porous silicon nanowires on top of porous silicon layer: <0.005 Ω-cm, Ag, 0.1 M H₂O₂, 3.5 M ethanol, 5 min. (d) Thin, spaghetti-like porous silicon nanowires on top of porous silicon layer: 0.0008-0.001 Ω-cm, Au, 0.1 M H₂O₂, 15 min. (e) Porous silicon layer: 0.01-0.02 Ω-cm, Ag, 0.1 M H₂O₂, 6.8 M ethanol, 5 min. (f) Polished silicon surface: 0.1-0.2 Ω-cm, Ag, 0.78 M H₂O₂, 5 min.
Figure 5.
Formation of nanostructures as a function of etching parameters. (a) Phase diagram of the different silicon nanostructure morphologies obtained by Ag assisted etch as a function of resistivity of the substrate and concentration of H₂O₂. (b) Phase diagram of the different silicon nanostructure morphologies obtained by Au assisted etch as a function of resistivity of the substrate and concentration of H₂O₂. (c) Si nanowire etch rate as a function of H₂O₂ concentration. Red squares indicate Au assisted etch of 0.01-0.02 Ω-cm substrates in 2.9 M HF, 0 M ethanol. Blue circles indicate Ag assisted etch of 0.01-0.02 Ω-cm substrates in 2.9 M HF, 0 M ethanol. (d) Si nanowires etch rate as a function of substrate resistivity. Red squares indicate Au assisted etch in 0.2 M H₂O₂, 2.9 M HF, 0M ethanol. Blue circles indicate Ag assisted etch in 0.2 M H₂O₂, 2.9 M HF, 0M ethanol. (e) Phase diagram of the different silicon nanostructure morphologies obtained by Ag assisted etch as a function of resistivity of the substrate and concentration of ethanol. (f) Si nanowires etch rate as a function of ethanol concentration. Red squares indicate Au assisted etch of 1-10 Ω-cm substrates in 0.1 M H₂O₂, 2.9 M HF. Blue circles indicate Ag assisted etch of 0.1-0.2 Ω-cm substrates in 0.1 M H₂O₂, 2.9 M HF.
Figure 6.
The difference in pore structure between porous nanowires and porous nanowires on porous silicon film is a result of a different etch mechanism. Cross sectional scanning electron micrograph of the base of: (a) Porous silicon nanowire: $<0.005 \, \Omega \cdot \text{cm}$, Ag, $0.1\, \text{M} \, \text{H}_2\text{O}_2$, 60min. Porosification occurs after the nanowire wall is formed, the porous structure is from the nanowire wall towards its major axis and does not fully extend to the base; (b) Porous silicon nanowire on porous silicon layer: $<005 \, \Omega \cdot \text{cm}$, Au, $0.4\, \text{M} \, \text{H}_2\text{O}_2$, 15 min. The porous structure is parallel to the nanowire wall and extends as continuous pores into the porous silicon film beneath. The silicon is first porosified and the nanowires walls are etched in the porous layer. The metal nanoparticles are localized at the top of the porous silicon film indicating that they do not catalyze porosification. (c) Schematic depiction of the etch mechanism for $C_i \cong C_e$. The metal nanoparticles etch into the solid silicon while the ions form pores orthogonal to the wall surface exposed to the electrolyte. During the elapsed time $\Delta t$ the porosification front has moved a distance $\Delta x_p$ and the nanowire etch front has moved a distance $\Delta x_e$. (d) Schematic depiction of the etch mechanism for $C_i > C_e$. The metal nanoparticles etch the nanowires into the porous silicon layer formed by the ions.