NANO
LETTERS

2005
Vol. 5, No. 3
457−460

Controlled Growth of Si Nanowire Arrays for Device Integration

Allon I. Hochbaum, Rong Fan, Rongrui He, and Peidong Yang*

Department of Chemistry, University of California, and Materials Science Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720

Received December 3, 2004; Revised Manuscript Received January 11, 2005

ABSTRACT

Silicon nanowires were synthesized, in a controlled manner, for their practical integration into devices. Gold colloids were used for nanowire synthesis by the vapor–liquid–solid growth mechanism. Using $SiCl_4$ as the precursor gas in a chemical vapor deposition system, nanowire arrays were grown vertically aligned with respect to the substrate. By manipulating the colloid deposition on the substrate, highly controlled growth of aligned silicon nanowires was achieved. Nanowire arrays were synthesized with narrow size distributions dictated by the seeding colloids and with average diameters down to 39 nm. The density of wire growth was successfully varied from ∼0.1–1.8 wires/μm^2. Patterned deposition of the colloids led to confinement of the vertical nanowire growth to selected regions. In addition, Si nanowires were grown directly into microchannels to demonstrate the flexibility of the deposition technique. By controlling various aspects of nanowire growth, these methods will enable their efficient and economical incorporation into devices.

Silicon nanowires (SiNWs) have been identified as useful building blocks for nanoscale electronic[1−3] and thermoelectric devices.[4,5] To realize their full potential in applications, however, SiNW must be integrated efficiently and economically into various device architectures. Devices have been constructed around single, or several dispersed SiNWs,[1−9] and methods have been developed to manipulate as-grown nanowires into geometries amenable to large-scale device fabrication.[10,11] Alternatively, controlled growth of SiNWs in predetermined configurations would eliminate much of the processing associated with device fabrication. Furthermore, vertical growth (perpendicular to the substrate) would allow three-dimensional integration for more complex structures, such as vertical field-effect transistor (VFET) arrays.[12] Such arrays could afford higher transistor densities and novel 3-dimensional logic or memory architectures.

The vapor−liquid−solid (VLS) growth mechanism, studied in detail in the 1960s and 70s by Wagner et al. and Givargizov,[13−15] is an ideal synthetic technique to control SiNW growth.[16,17] VLS growth by chemical vapor deposition (CVD) can produce epitaxially aligned, single-crystalline wires. Specifically, SiNWs may be grown via VLS process using gold thin films.[18,19] Metal thin film, however, does not provide good diameter control of the resulting wires due to the randomness of the film breakup at reaction temperatures. Also, precise growth and epitaxial alignment of SiNWs has only been achieved using lithographically defined regions of SiNW growth by thin film evaporation.[20,21] These methods employ expensive processing techniques with limited control over nanowire size and density.

On the other hand, gold colloids can be used to produce well-dispersed and diameter-controlled SiNWs, although simultaneous control over the size, position, and epitaxial growth has not been achieved previously.[22,23] In this paper we demonstrate methods to grow vertically aligned SiNW with controlled dimensions and specific placement by the conventional VLS−CVD synthesis. Using a thin polyelectrolyte layer, gold colloids are electrostatically attracted to and immobilized on the substrate to act as seeds for Si nanowires grown using the VLS−CVD method. The diameter of the colloids precisely controls the nanowire diameter. The colloid solution concentration controls the density of growth. Microcontact printing of the polyelectrolyte layer confines wire growth to patterned regions. Moreover, these versatile techniques facilitate incorporation of vertically aligned SiNWs into more complex systems, such as microfluidic channels.

In general, Au colloids are used to define the diameter and position of the SiNWs. Subsequent wire growth occurs along the ⟨111⟩ direction and is vertical due to the epitaxial growth of Si wires from the binary liquid droplet onto the underlying substrate, a Si (111) wafer, as previously shown.[8,14,24] The colloids were immobilized on the wafer surface using a previously developed technique.[22,25] A thin layer of polyelectrolyte adsorbed onto the substrate surface by a quick immersion in 0.1 wt % poly-L-lysine. After rinsing with DI water, the substrates were immersed in the Au nanoparticle solution (10^{10}−10^{11} particles/mL, Ted Pella

---

* Corresponding author. E-mail: p_yang@uclink.berkeley.edu.

10.1021/nl047990x CCC: $30.25

Inc.). The polymer possesses a net positive charge in aqueous solution at neutral pH and hence adsorbs onto the substrate due to its electrostatic attraction to deprotonated hydroxyl groups on the silica layer. Consequently the polymer film presents a positively charged surface to the negatively charged Au colloids in aqueous solution, attracting them to the surface. Following a final rinse with DI water and drying, the substrates were used for nanowire growth in a CVD furnace as reported previously.[8]

$SiCl_4$ was used as the precursor molecule for SiNW growth in the CVD system. Growth of various substrates seeded with Au colloids was conducted at temperatures between 800 and 850 °C. H_2(10%) in argon was used as the carrier gas flowed through the Si precursor bath and into the reaction tube. The substrates were cleaned with acetone and IPA before polymer and colloid deposition. The polymer was presumably ashed by the high reaction temperatures and a reducing H_2 environment. Gaseous HCl, a byproduct of $SiCl_4$ decomposition in the reaction tube, etched the oxide layer on the Si surface, presenting a clean Si crystal surface to precipitating Si from the binary liquid droplet. Epitaxial deposition of Si at this interface induced growth direction alignment of the nanowire with the crystal face of the Si wafer. Consequently, such alignment is not possible using other CVD precursors, such as SiH_4, without separately adding HCl gas[20,21] or taking special precautions to remove the oxide layer before SiNW synthesis. SiNWs synthesized by the above method on a Si (111) substrate yielded vertically aligned, single-crystalline wires, as observed by scanning and transmission electron microscopy (SEM and TEM). Wires aligned along the three [−111] directions were also observed, especially in syntheses using smaller colloidal catalysts, but the gas flow rate and reaction temperature were optimized to preferentially grow vertical wires for each colloid system.

Au colloids are ideal seeds for controlling the SiNW diameter: They act as the seeding metal for nanowire growth by the VLS process, and Au colloids may be synthesized or obtained commercially with relatively narrow size distributions. Since each colloid seeds the growth for one nanowire, aligned nanowires can be grown with narrow size distributions approaching those of the seed particles. Hence, by seeding wire growth with colloids of different average size, we were able to precisely control the average diameter of the SiNW arrays, as seen in Figure 1b, d, and f. Size distributions of both colloids and nanowires were determined from TEM micrographs. SiNWs grown from Au colloids of 50 (56 ± 5.0), 30 (30 ± 3.3), and 20 (20 ± 2.1) nm diameters were 93 ± 7.4, 43 ± 4.4, and 39 ± 3.7 nm in diameter, respectively. Extensive TEM (Figure 1g) characterization indicates that these wires are single crystalline in nature. We would like to emphasize that although monodisperse silicon nanowires can be synthesized using monodispersed Au colloids as seeds,[24] epitaxially grown, monodispersed silicon nanowires were grown here for the first time through this chloride based CVD process.

The SiNWs were wider than their respective seed particles due to the influx of Si into the colloids and alloy formation during the synthesis. The seed droplets swell in size until the critical supersaturation concentration is reached,[17] at which point Si begins precipitating on the Si (111) surface below. The interface between the Au−Si droplet and the substrate determines the area of precipitation of Si, and thus the SiNW diameter. Despite their larger size, however, the nanowires have approximately the same relative standard deviation of diameter as the colloidal solutions used to seed their growth. The standard deviations of the 50, 30, and 20 nm colloids used in this study are ± 8.8%, 11%, and 11% of the average size, respectively. The standard deviations of the wires grown from these colloids are ± 7.9%, 10%, and 9.5% of the average size, respectively. These data suggest that precise diameter control of nanowires grown by this method is limited only by the size distribution of the seed particles. Hence, appropriate colloidal solutions could be used to grow monodisperse nanowire arrays.

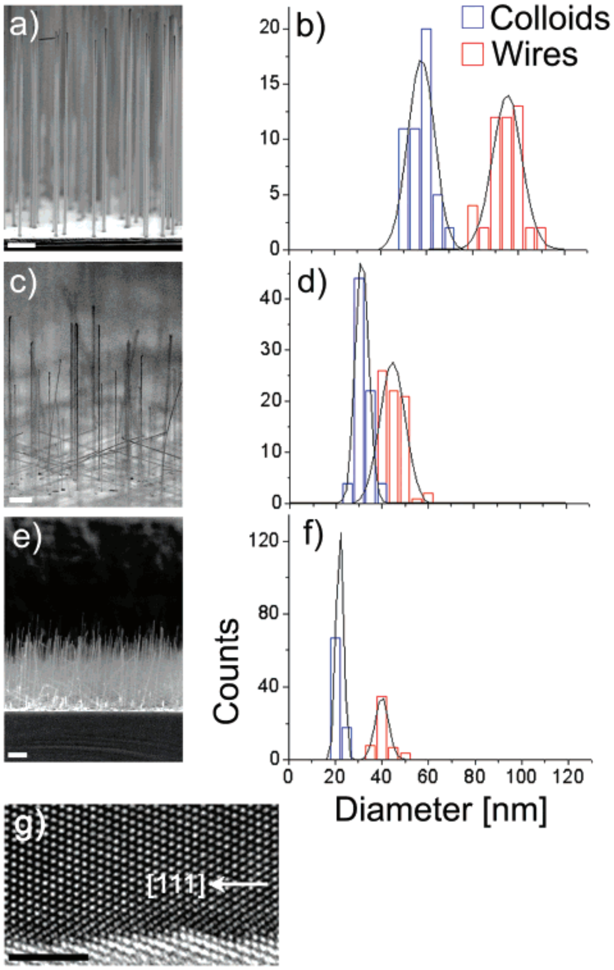

Figure 1. (a, c, e) Cross-sectional images of nanowire samples grown from 50, 30, and 20 nm (nominally) Au colloids, respectively. Scale bars are 1 μm. (b, d, f) Size distributions of Au colloids and resulting SiNW diameters. (g) High-resolution transmission electron microscopy image of a single crystalline Si nanowire. Scale bar is 3 nm.

The density of nanowire growth is also critical to device function. By varying the concentration of the seeding solution (using 50 nm Au colloids as example here), we were able to control the seeding density on the substrate surface. The graph in Figure 2 shows the relationship between nanowire

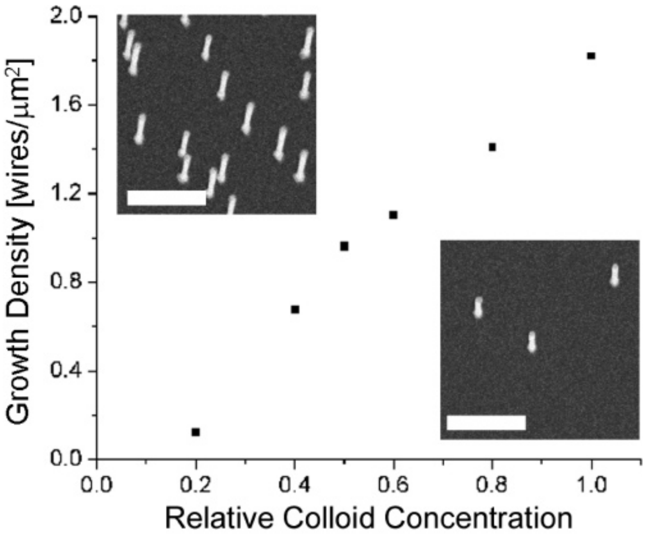

Figure 2. SiNW growth density dependence on the relative concentration of the seeding solution. All colloid solutions were diluted from the same stock solution. Insets show typical nanowire growth at 4/5 (top left) and 2/5 dilution (bottom right). Scale bars are 1 μm.

growth density, as determined from SEM images, and dilution of the gold colloid stock solution. Wires were seeded with densities ranging over an order of magnitude, from ∼0.1−1.8 wires/μm^2. In general, a good 1-to-1 nanoparticle/nanowire ratio can be achieved, although it was observed that optimal growth conditions varied slightly with nanowire seeding density.

Spatial control over SiNW growth was achieved by patterning regions of seed particles using microcontact printing. A poly(dimethylsiloxane) (PMDS) stamp was made using a photoresist master of 2 μm lines with 2 μm separation, and the pattern was transferred to the substrate by previously established techniques[26] (Figure 3a). The stamp was "inked" with the poly-L-lysine solution by the same method described above for deposition on the Si substrates. The polymer pattern was transferred to a Si wafer by placing the stamp on the substrate and heating at 70 °C for 5 min. The patterned substrate was immersed in the 50 nm Au colloid solution for a short time, such that colloids only adhered to the polyelectrolyte and not the bare Si. Nanowires were synthesized on these substrates by the same CVD method discussed above. The resulting growth, seen in Figure 3b and c, is strictly confined to the regions of poly-L-lysine deposition. The plane-view SEM image (Figure 3c) shows a small part of the pattern, which is consistent over several square millimeters − the extent of the stamped area that was immersed in the colloid solution.

In addition, this colloid-seeded growth method represents a convenient way to incorporate nanowires into other systems, such as microfluidic systems. The microchannels used were 8 μm deep and 40−100 μm wide. They were etched into a Si (111) wafer by deep reactive ion etching (DRIE) using SF_6/O_2 as the etchant and C_4F_8 as the sidewall passivation gas. The middle portion of a microchannel array was covered with an O_2 plasma-treated piece of blank PDMS. The PDMS encloses the microchannels by adhering to the top Si (111) surface. The colloid deposition method resembles those discussed above. First, a droplet of the poly-L-lysine solution was placed on one end of the microchannel array, touching the PDMS. The solution was transported by capillary action to the open end of the channels. After rinsing in DI water, the PDMS was replaced and a droplet of 50 nm Au colloid solution was placed where the polymer solution had been. In the same manner as before, the solution flowed to the opposite end of the channels, and then the substrate was rinsed again. The wires were grown directly in the channels under the same conditions as previous syntheses.

As can be seen from Figure 4, nanowire growth and vertical alignment were not affected by either the roughness of the floor of the channel − due to etching − or any changes in precursor gas flow dynamics near the channel walls.

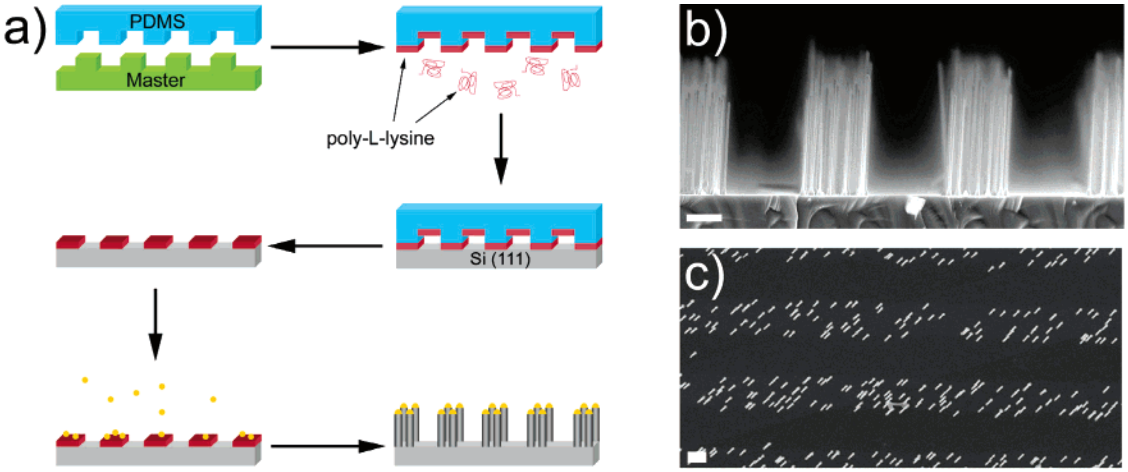

Figure 3. (a) Schematic of PDMS patterning of Au colloids. Briefly, a PDMS stamp is molded to the relief pattern of a photoresist master. After curing the polymer, the stamp is removed from the master and "inked" with a solution of poly-L-lysine. The stamp pattern is transferred to the Si (111) substrate, which is then immersed in the Au colloid solution. The colloid-patterned substrate is grown using the conventional VLS−CVD synthesis, resulting in a corresponding pattern of SiNW arrays. (b) Cross-sectional SEM image of PDMS patterned SiNW growth, and (c) plane-view SEM image of the same. Scale bars are 1 μm.

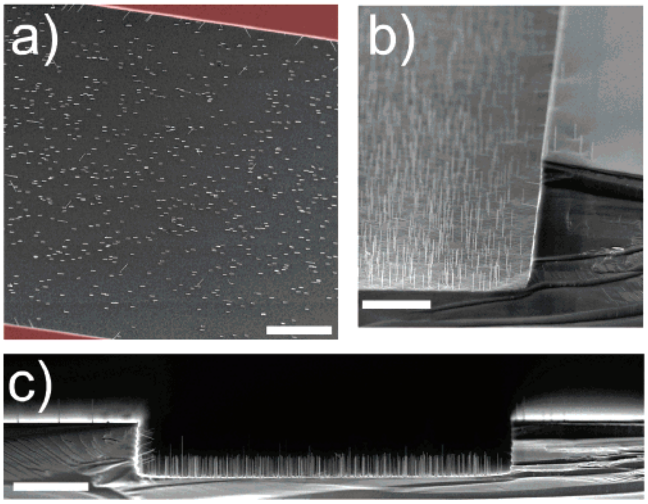

Figure 4. SiNWs grown directly in a microchannel. (a) A plane-view SEM image where the top Si surface has been falsly colored to guide the eye. Nanowire growth is almost completely confined to the floor of the channel. (b) A ∼45° tilt and (c) cross-sectional view SEM image of the same. Scale bars are 10 μm.

Furthermore, the PDMS restricted gold colloid deposition predominantly to the floor of the microchannel. There is little to no nanowire growth on top surface of the substrate, so the microchannels may be resealed with PDMS to function as a microfluidic device, such as for macromolecular separation based on SiNWs as diffusion barriers.

In summary, using directed colloid seeding for VLS−CVD SiNW synthesis provides precise control over nanowire diameter, growth density, and spatial distribution. At the same time, the $SiCl_4$ precursor is highly effective for the growth of vertically aligned, single-crystalline SiNWs. Moreover, these techniques facilitate the direct integration of nanowires into complex systems such as microfluidic devices. The versatility of our growth control methods stems from the use of $SiCl_4$ as the gas phase precursor. Without separately incorporating HCl gas,[20,21] other Si precursors (e.g., SiH_4) do not offer such flexibility of substrate preparation and vertical SiNW alignment. Specifically, the aligned growth of SiNWs makes this process ideal for fabricating array devices, such as VFET circuits and 2-dimensional photonic crystals. Additionally, these arrays may serve as scaffolding for the deposition of other materials for an even wider range of applications. Such in-place growth control will aid the incorporation of nanowires into devices.

Acknowledgment. This work was supported by DOE and NSF. P.Y. is an Alfred P. Sloan Research fellow. A.H. thanks the NSF IGERT program for predoctoral fellowship support. We thank the National Center for Electron Microscopy for the use of their facilities.

References

(1) Cui, Y.; Duan, X.; Lieber, C. M. *J. Phys. Chem. B* **2000**, *104*, 5213.
(2) Yu, J.-V.; Chung, S.-W.; Heath, J. R. *J. Phys. Chem. B* **2000**, *104*, 11864.
(3) Cui, Y.; Lieber, C. M. *Science* **2001**, *291*, 851.
(4) Li, D.; Wu, Y.; Fan, R.; Yang, P.; Majumdar, A. *Appl. Phys. Lett.* **2003**, *83*, 3186.
(5) Li, D.; Wu, Y.; Kim, P.; Shi, L.; Yang, P.; Majumdar, A. *Appl. Phys. Lett.* **2003**, *83*, 2934.
(6) Cui, Y.; Wei, Q.; Park, H.; Lieber, C. M. *Science* **2001**, *293*, 1289.
(7) Zhong, Z.; Wang, D.; Cui, Y.; Bockrath, M. W.; Lieber, C. M. *Science* **2003**, *302*, 1377.
(8) Fan, R.; Wu, Y.; Li, D.; Yue, M.; Majumdar, A.; Yang, P. *J. Am. Chem. Soc.* **2003**, *125*, 5254.
(9) Abramson, A. R.; Kim, W. C.; Huxtable, S. T.; Yan, H.; Wu, Y.; Majumdar, A.; Tien, C,-L.; Yang, P. *J. Microelectromech. Syst.*, **2004**, *13*, 505,
(10) Tao, A.; Kim, F.; Hess, C.; Goldberger, J.; He, R.; Sun, Y.; Xia, Y.; Yang, P. *Nano. Lett*. **2003**, *3*, 1229.
(11) Whang, D.; Jin, S.; Wu, Y.; Lieber, C. M. *Nano Lett.* **2003**, *3*, 1255.
(12) Ng, H.; Han, J.; Yamada, T.; Nguyen, P.; Chen, Y. P.; Meyyappan, M. *Nano Lett.* **2004**, *4*, 1247.
(13) Wagner, R. S.; Ellis, W. C. *Appl. Phys. Lett.* **1964**, *4*, 89.
(14) Wagner, R. S. VLS Mechanism of Crystal Growth, in *Whisker Technology*, Levitt, A. P., Ed.; Wiley-Interscience: New York, 1970; pp 47−119.
(15) Givargizov, E. I. *J. Cryst. Growth* **1975**, 31, 20.
(16) Morales, A. M.; Lieber, C. M. *Science* **1998**, *279*, 208.
(17) Wu, Y.; Yang, P. *J. Am. Chem. Soc.* **2001**, *123*, 3165.
(18) Wu, Y.; Yan, H.; Huang, M.; Messer, B.; Song, J.; Yang, P. *Chem. Eur. J.* **2002**, *8*, 1260.
(19) Westwater, J.; Gosain, D. P.; Tomiya, S.; Usui, S.; Ruda, H. *J. Vac. Sci. Technol. B* **1997**, *15*, 554.
(20) Gangloff, L.; Minoux, E.; Teo, K. B. K.; Vincent, P.; Semet, V.; Binh, V. T.; Yang, M. H.; Lacerda, R. G.; Bu, I. Y. Y.; Pirio, G.; Schnell, J. P.; Pribat, D.; Hasko, D. G.; Amaratunga, G. A. J.; Milne, W. I.; Legagneux, P. *Nano Lett.* **2004**, *4*, 1575.
(21) Saif Islam, M.; Sharma, S.; Kamins, T. I.; Williams, R. S. *Nanotechnology* **2004**, *15*, L5.
(22) Cui, Y.; Lauhon, L. J.; Gudiksen, M. S.; Wang, J.; Lieber, C. M. *Appl. Phys. Lett.* **2001**, *78*, 2214.
(23) Wu, Y.; Cui, Y.; Huynh, L.; Barrelet, C. J.; Bell, D. C.; Lieber, C. M. *Nano Lett.* **2004**, *4*, 433.
(24) Wu, Y.; Fan, R.; Yang, P. *Nano Lett*. **2002**, *2*, 83.
(25) Vesenka, J.; Manne, D.; Giberson, T. M.; Henderson, E. *Biophys. J.* **1993**, *65*, 992.
(26) Xia, Y.; Whitesides, G. M. *Annu. Rev. Mater. Sci.* **1998**, *28*, 153.

NL047990X