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Rational Growth of Branched and Hyperbranched Nanowire Structures

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ABSTRACT

Branched and hyperbranched nanowire structures were synthesized via a multistep nanocluster-catalyzed vapor−liquid−solid approach. Scanning electron microscopy studies of silicon nanowire structures prepared in this way confirmed the formation of branched nanostructures and showed that the branch density could be controlled by the nanocluster catalyst concentration. This same approach was also used to grow branched gallium nitride nanowires. High-resolution transmission electron microscopy studies of the branched silicon nanowire structures revealed that the branches grew epitaxially as single-crystal nanowires from the silicon nanowire backbone. In addition, hyperbranched silicon nanowire structures were prepared in a controlled manner by repeating the catalyst deposition and nanowire growth steps. The ability to prepare rationally branched and hyperbranched nanowires should open up new opportunities for both fundamental research and applications, including three-dimensional nanoelectronics.

Semiconductor nanowires (NWs) are attractive building blocks for the "bottom-up" assembly of nanoelectronic and nanophotonic systems.[1] The ability to control the electronic properties of nanowires in a predictable manner during synthesis[2,3] has enabled reproducible fabrication of a number of nanodevices based on single NWs, including field effect transistors (FETs),[3−6] photodetectors,[7] and sensors.[8] NWs with distinct properties have also been assembled into a scalable crossed-NW architecture[1] to yield a wider range of functional devices and circuits, such as transistors,[4,9,10] light-emitting-diodes (LEDs),[6,11] logic gates,[4,9] and address decoders.[10] In a similar manner, the controlled elaboration of NW structure through the growth of NW superlattices[12,13] and radial heterostructures[14] also enables enhanced functionality as single NW LEDs[12] and novel high mobility FETs,[14] respectively.

Conceptually, branched NWs offer another approach for increasing structural complexity and enabling greater function.[15] Alivisatos and co-workers have reported the solution-based synthesis of tetrapod or branched nanocrystals of cadmium telluride with control of the diameter of identical arms.[16] Branched NW and nanoribbon structures, which are formed by vapor transport and condensation during growth, have also been reported.[17] However, these latter studies have exhibited only limited control over the density and size of nanoscale branches that ultimately are central to the rational design of building blocks for devices. To explore the potential of the branched NW architecture, we report here a general approach that enables the controlled synthesis of branched and hyperbranched NW structures. Our approach exploits a multistep nanocluster-catalyzed vapor−liquid−solid (VLS) growth process in which the nanocluster diameter and density, which define the branch diameter and density, and vapor phase reactants can be independently varied at each step.

Figure 1 outlines our approach for the synthesis of branched and hyperbranched NWs, and exploits the fact that diameter controlled growth of a wide range of NWs, including group IV,[2] III−V,[6,18] and II−VI[18,19] materials, is possible using the nanocluster-mediated VLS method.[1,2] The key steps in our approach are as follows. First, a NW backbone of specific diameter and composition is prepared by nanocluster-mediated VLS growth. Second, nanocluster catalysts of defined diameter are deposited on the backbone, and then first-order branches are grown by the VLS process. Third, the branch growth steps can be repeated one or more times to yield higher order or hyperbranched NW structures.

The basic features of this new approach were demonstrated with growth of silicon-based branched nanostructures. First, SiNWs, which serve as backbones, were synthesized via gold nanocluster-mediated VLS growth process using silane as the reactant.[2,5,20] Gold nanoclusters with diameters equal to or smaller than SiNWs produced in the first step were then deposited from solution onto the NW backbones, and SiNW branches were grown in the same way as the initial

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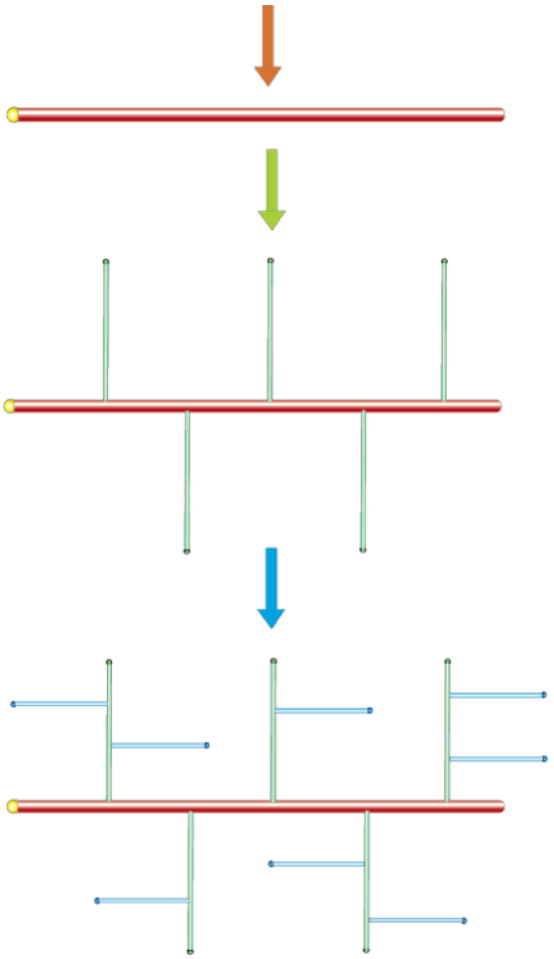

Figure 1. Schematic illustrating the multistep syntheses of branched and hyperbranched NW structures. Red, green, blue arrows/colors signify the growth of the backbone, first generation, and second generation NWs, respectively.

backbone.[20] Figure 2a−2d shows representative scanning electron microscopy (SEM) images of branched SiNW structures prepared using increasing concentrations of gold nanoclusters during the deposition process. The images show clearly branched nanostructures and are distinct from images of crossed NWs.[9] Analysis of a large number of images also shows that the branched nanowires are produced with very good purity by our approach. In addition, the images show that the NW branch density increases directly with the concentration of deposited gold nanoclusters, and hence, demonstrate that our approach can control this important structural parameter. Last, the SEM images show that the SiNW branches grow within a range of angles, ca. 60°−70°, with respect to the backbone.[21] The specific angles indicate that branch growth is epitaxial; this point is discussed in detail below.

GaN NWs, which are of considerable interest as building blocks for nanophotonic devices,[11,22] also have been prepared as branched nanostructures by our approach. SEM images of branched GaN NWs prepared following deposition of 0.001 and 0.1 M nickel catalyst precursor (Figure 2e and 2f, respectively) show clearly that the NW branch density can be controlled in our multistep growth process. These results contrast recent studies of branched ZnO nanowires

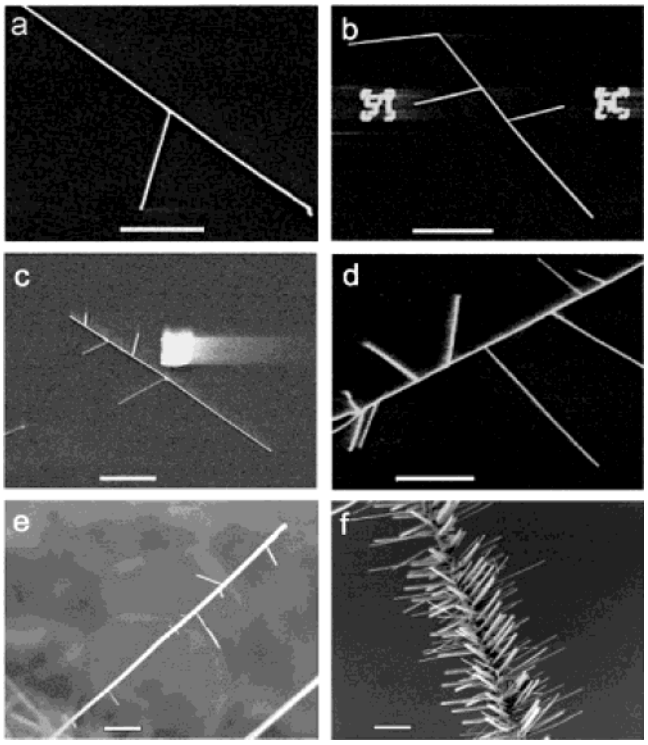

Figure 2. SEM images of branched nanowire structures. Branched SiNW structures prepared following deposition of gold nanoclusters from (a) 1:20, (b) 1:8, (c) 1:3, and (d) 1:1 diluted stock solutions and subsequent growth.[20] SEM images of branched GaN NW structures prepared following deposition of (e) 0.001 M and (f) 0.1 M nickel catalyst precursor solution. Scale bars are all 1 μm.

and nanoribbons prepared in a single-step process[17] that makes the control of branch density more difficult. The growth of branched GaN NWs with controlled branch density, together with the data above for branched SiNWs, further suggests that our approach should be quite general and thereby could provide access to branched NW nanostructures with a wide range of compositions.

In addition, we have used transmission electron microscopy (TEM) to characterize the structure of the branched SiNWs in more detail. These data (Figure 3) demonstrate several key points. First, the diameter of the branches, 22 nm, and backbone, 30 nm, are consistent with the diameters of the gold nanoclusters used to mediate their growth: 20 and 30 nm, respectively. These TEM results show that our approach can yield branched structures in which the diameters of the different NWs are controlled in a manner similar to previous studies of single-step nanowire growth.[2] Second, the lattice-resolved data (Figure 3b−3d) show that the branched SiNWs have single-crystal structures with clean backbone-to-branch junctions that are consistent with epitaxial branch growth. To characterize further the branch structures we analyzed the reciprocal lattice peaks determined from two-dimensional Fourier transforms of the lattice-resolved images of the backbone (inset, Figure 3b) and branch (inset, Figure 3c).[23] The indexed reciprocal lattices show that the [-111] direction was aligned with the backbone axis and the [-11-1] direction was aligned with the branch axis. The backbone−branch angle determined from the

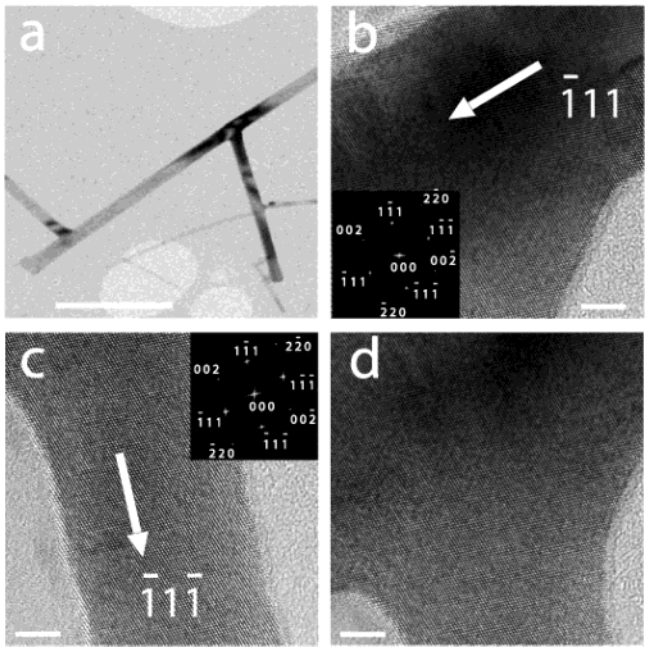

Figure 3. (a) TEM image of a branched NW structure showing two branches; scale bar is 250 nm. Lattice-resolved TEM images of the (b) backbone, (c) branch, and (d) junction. The NWs growth axes are indicated by the white arrows. Scale bars are 5 nm. Insets in (b) and (c) are reciprocal lattices determined from two-dimensional Fourier transforms of the respective images.

reciprocal lattice peaks, 72.3°, is consistent with the 70.5° angle between these two directions for the silicon crystal structure. These results demonstrate that SiNW branches are epitaxial, and thus we expect these new structures could yield interesting functional devices.

Last, our approach can be extended as suggested in Figure 1 to produce substantially more complex NW architectures. To illustrate this point, hyperbranched SiNW structures were synthesized by a three-step growth procedure in which 40, 20, and 10 nm gold nanoclusters were used to catalyze the VLS growth of the SiNWs comprising the backbone, first generation, and second generation branches, respectively. Significantly, an image of a representative nanostructure prepared in this way (Figure 4) shows clearly these first and second generation branches, which are unambiguous due to the differences in NW diameters nucleated using 20 and then 10 nm diameter nanoclusters. This image also shows a 10 nm branch on the backbone, which can be attributed to growth during the second branch step. This observation represents a limitation of the present work, which potentially can be overcome by developing more selective nanocluster catalyst deposition methods.

In summary, we have described a rational approach to the growth of branched and hyperbranched NW structures in which the branch NW composition, diameter, and density can be controlled using a multistep nanocluster-catalyzed VLS process. We have demonstrated this basic approach with the growth of branched Si and GaN NW structures, as well as with more complex hyperbranched SiNW structures. Detailed TEM studies of the branched SiNW structures demonstrate that the branches grow epitaxially and thus

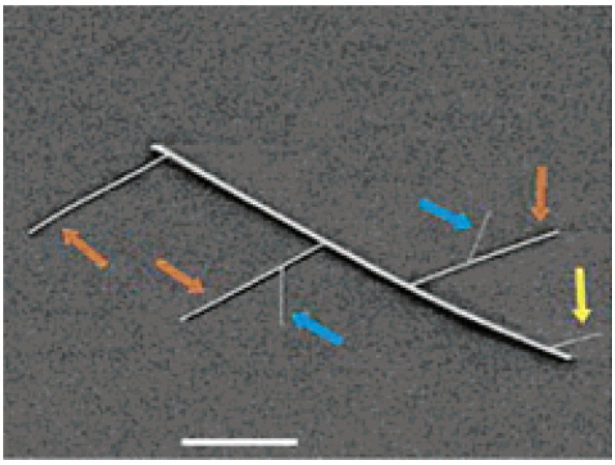

Figure 4. SEM image of a hyperbranched SiNW structure. The first-generation and second-generation branches are indicated by orange and blue arrows, respectively. Yellow arrow indicates a 10 nm SiNW (from second generation growth) grown from the backbone. Scale bars is 1 μm.

suggest the potential of this approach for creating a range of electronically active devices. Indeed, preliminary transport studies of branched SiNW structures consisting of p-type backbones and n-type branches indicate that p−n diodes and junction FETs can be obtained from these nanostructures.[24] The ability to introduce active electronic and optoelectronic junctions into branched and hyperbranched NW structures should open up many opportunities in the future, including three-dimensionally interconnected computing structures analogous to the brain.

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(20) SiNW backbones were grown by dispersing gold nanoclusters (Ted Pella) on an oxidized silicon wafer. The substrate was placed in a horizontal quartz reactor, heated to 440 °C under argon, followed by 2.5 sccm SiH_4, 1.5 sccm B_2H_6, and 10 sccm Ar for 20 min, with the growth pressure maintained at 40 Torr. SiNW branches were grown in a similar way following the deposition of gold nanoclusters onto the nanowire backbone from ethanol solution. The branches were prepared using 10, 20, 30, or 40 nm diameter gold nanoclusters with the diameter equal to or smaller than the diameter used to grow the preceding nanowire (i.e., backbone or first generation branch). Ethanol suspensions of the branched and hyperbranched SiNWs were prepared by gentle sonication of the growth substrates in ethanol. These solutions were deposited onto Si substrates for SEM studies.
(21) The angles determined from these SEM images can have substantial uncertainty since the orientation of the backbone and branch relative to the image plane is not known. Accurate angle measurements can, however, be made from lattice-resolved TEM images.
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