Communication

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J. Am. Chem. Soc., **2008**, 130 (32), 10488-10489 • DOI: 10.1021/ja8037382 • Publication Date (Web): 19 July 2008

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Published on Web 07/19/2008

Vertical Growth of Ge Nanowires from Biotemplated Au Nanoparticle Catalysts

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One-dimensional (1D) nanostructures, such as semiconductor nanowires (SCNWs), are attracting significant attention for their potential applications in nanoelectronic and photonic devices. It is expected that the functional properties of SCNWs will be enhanced by collective effects associated with arranging high-density NWs with well-defined diameters and orientations in predetermined configurations. In particular, vertically aligned NW architectures are needed for the realization of three-dimensional (3D) integrated devices such as vertical field-effect transistor arrays[1−3] and room-temperature ultraviolet nanolasers.[4] However, as semiconductor devices are further miniaturized, higher-resolution processes are required for the position-controlled, nanopatterned growth of NWs. Electron-beam lithography and scanning probe lithography are generally employed to grow NWs at well-defined locations through the patterning of the catalyst on the substrate. Still, these line-by-line pattern-generation techniques are relatively slow and involve high fabrication costs. Bottom-up strategies, including nanosphere lithography, block copolymers, porous alumina templates, and biological-based templates such as surface-layer proteins (S-layers), are emerging as promising catalyst-positioning approaches.[5] This communication presents for the first time the controlled growth of high-density, vertically oriented NWs with monodispersed diameters and spacings via S-layer biotemplating of gold nanoparticle (AuNP) catalysts.

S-layers are 2D crystalline arrays of proteins found on the outermost surfaces of many bacteria. Depending on the bacteria species, S-layers exhibit oblique, square, or hexagonal lattice symmetries with unit cell dimensions in the range of 3 to 30 nm.[6] The regularly spaced affinity sites defined by the periodic arrangement of identical protein subunits have been exploited to fabricate ordered arrays of metallic[7] and semiconductor[8] NPs and nanopillars[9] in a parallel fashion. In the work presented here, S-layer sheets were extracted from *Deinococcus radiodurans*, adsorbed onto hydrogen-terminated Ge(111) substrates, and used for the templating of presynthesized citrate-capped AuNPs of various diameters (see the Supporting Information). All the samples were outgassed overnight at 200 °C in a cold-wall chemical vapor deposition (CVD) system. Germanium nanowires (GeNWs) were grown for 5 min following a two-step process in which the temperature was dropped from 425 to 375 °C upon introduction of GeH_4 in H_2 (flow rate 188 sccm; partial pressure 0.9 Torr).

Figure 1 shows vertically aligned GeNWs grown from biotemplated 5, 10, and 20 nm AuNP catalytic seeds. To the best of our knowledge, there is only one report to date where small AuNP catalysts (10 nm) were employed in the vertical growth of GeNWs from Ge(111) substrates.[10] In our study, the NWs showed no tapering and were very uniform in diameter and length (~1.5 μm).

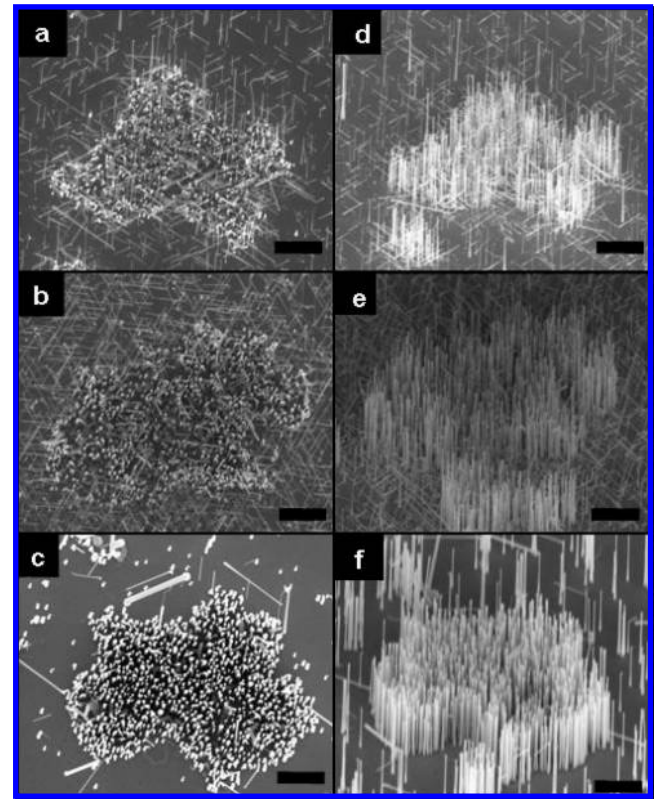

Figure 1. (a−c) Top-view SEM images and (d−f) corresponding 30° tilt views of Ge nanowires grown from biotemplated (a, d) 5, (b, e) 10, and (c, f) 20 nm presynthesized Au nanoparticles. Scale bars = 1 μm.

The high-density areas of vertically oriented NWs correspond to NWs grown from AuNPs adsorbed on S-layer sheets. Nontapered, scattered NWs of similar lengths were also observed in the background regions; these NWs grew from sparsely dispersed AuNPs nonspecifically adsorbed on the substrate. These results demonstrate that under the CVD conditions used, neither the catalyst size nor the protein organic layer hindered nucleation and epitaxial growth of the GeNWs.

Further, the vertical <111> epitaxial growth direction is strongly preferred for GeNWs grown from biotemplated AuNPs. This contrasts with results for GeNWs grown from AuNPs under the same growth conditions but without the protein template, where all four available NW <111> epitaxial growth orientations are populated (Figure 2a−c). The role of the protein template in controlling NW epitaxy is uncertain; however, we speculate that the preferential growth of vertical NWs may be related to a synergetic effect due to the proximity of NWs within the protein template. The surrounding protein, or its remnant, may also provide

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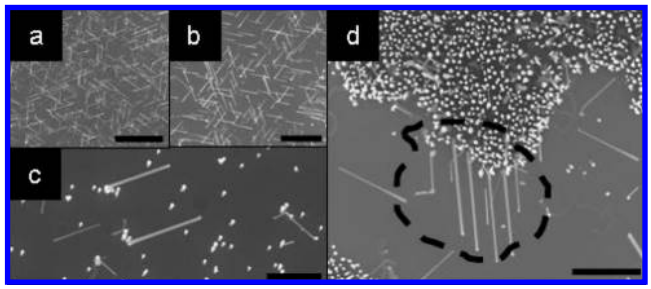

Figure 2. Top-view SEM images of Ge nanowires grown from (a) 5, (b) 10, and (c) 20 nm AuNPs adsorbed on bare Ge(111) substrates. (d) Nonvertical growth of nanowires is typically observed at the boundaries of the biotemplate. Scale bars = 1 μm.

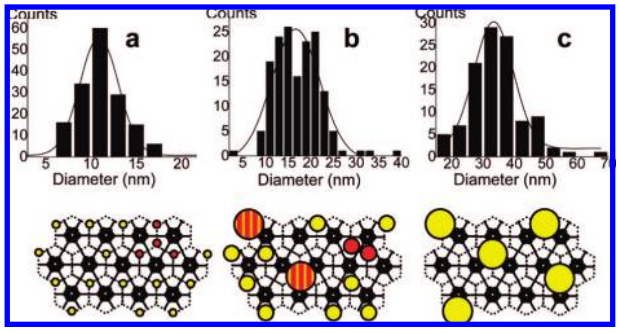

Figure 3. Histograms of measured diameters for Ge nanowires grown from (a) 5, (b) 10, and (c) 20 nm Au colloids. The array of AuNPs expected for each case is depicted as a schematic below the corresponding histogram.

a framework that keeps the AuNPs from fully wetting the Ge substrate at the onset of growth, thus preventing the formation of inclined facets leading to nonvertical growth orientations. This is in accordance with the nonvertical growth of NWs that is generally observed at the boundaries of the protein template (Figure 2d) due to a less-effective binding of the AuNPs. Still, further work is required in order to fully elucidate the role of the protein in the selective nucleation of vertical growth.

Diameter-dependent growth directions of SiNWs[11,12] and GeNWs[13,14] have been demonstrated: NW growth in the <111> direction is preferred for NW diameters ≥20 nm. This is in accordance with the high density (NWs/μm^2) of vertically oriented NWs observed here for NWs growing from biotemplated 20 nm AuNPs. Although 5 and 10 nm AuNPs led to higher coverages of biopatterned catalysts (Figure S2 in the Supporting Information), these NP biotemplates showed relatively lower yields of GeNWs. Nonetheless, the vertical NW densities achieved for NWs grown from 5, 10, and 20 nm AuNPs were 20, 30, and 70 NWs/μm^2, respectively. We believe that these are among the highest packing densities reported to date for the parallel synthesis of GeNWs grown from Au colloids below 20 nm in size.

Mean diameters of 11, 17, and 33 nm were observed for GeNWs grown from the nominal 5, 10, and 20 nm AuNPs, respectively (Figure 3a−c). This increase in diameter is due to the expansion of the Au catalyst as it forms a AuGe liquid drop during the vapor−liquid−solid growth. Also, some NP coalescence can be expected as a result of the narrow distance between AuNPs in the S-layer biotemplate, leading to NWs with larger diameters.

Figure 3 depicts schematic representations of the hypothetical binding of NPs to the vertex regions of the hexagonal-packed intermediate (HPI) S-layer template. Our earlier TEM studies showed that because of electrostatic repulsions, adsorption of 5 and 10 nm AuNPs to the HPI layer tends to be favored at every second vertex point (Figure 3a,b schematics, yellow circles), with a mean interparticle spacing of ∼18 nm that correlates with the underlying S-layer lattice constant.[7,8] Even so, some AuNPs with a nearest-neighbor distance of ∼10.4 nm (vertex−vertex point distance) are observed to be randomly distributed across the protein template (Figure 3a,b schematics, red circles). Because of the close proximity of the NPs, agglomeration is more likely to occur with 10 nm AuNPs occupying neighboring vertex points in the protein template. This would lead to two populations of NWs with different diameters: NWs growing from a single AuNP and those from aggregates of two AuNPs (Figure 3b schematic, striped circles). This case is supported by the fact that the diameter distribution for NWs grown from 10 nm AuNPs is broader and has peaks separated by ∼10 nm (Figure 3b). For the adsorption of 20 nm AuNPs, further investigation is required in order to determine the specific binding sites and distribution. Since this NP size is greater than the lattice constant of the underlying protein layer, long-range periodicity is not anticipated (Figure S2). However, we believe that metal binding takes place at locations defined by the highly periodic arrangements of functional groups on the HPI layer. Moreover, we have previously demonstrated that different adsorption patterns of the Au catalyst arise, depending on the initial adsorption of particles relative to each other, the binding conditions of the bulk solvent phase (e.g., ionic strength), and the protein orientation, which is influenced by the surface chemistry (e.g., degree of hydrophobicity) of the substrate used.[7] We predict that the generation of NW arrays with long-range order and controlled interwire distance can be achieved by controlling these parameters. Currently, different CVD growth conditions and sample preparation procedures are being explored in order to faithfully transfer the highly ordered array structure of the S-layer-patterned catalysts into that of the synthesized NW arrays.

In summary, we have demonstrated for the first time the synthesis of high-density, vertically oriented Ge nanowires with precise control over the size and orientation via biotemplating of very small sized (5−20 nm) Au nanoparticle catalysts. We envision the applicability of this biotemplating approach to a variety of NWs and substrate materials.

Acknowledgment. The National Science Foundation (NSF-0403990), U.S. DOE, NNSA, the LDRD Program, and the Cornell Nanoscale Facility (NSF Grant ECS-0335765) supported this work.

Supporting Information Available: Materials and methods used for bacteria growth, protein extraction/purification, templating of AuNPs, growth of GeNWs, and TEM images of AuNP templates. This material is available free of charge via the Internet at http://pubs.acs.org.

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JA8037382