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# Diameter-Selective Synthesis of Semiconductor Nanowires

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Nearly monodisperse samples of single crystalline GaP nanowires have been synthesized with diameters of 10, 20, and 30 nm and lengths greater than 10 $\mu$m by exploiting well-defined gold colloids as catalysts in our laser catalytic growth (LCG) synthetic methodology.[1−4] Transmission electron microscopy (TEM) studies of nanowires prepared in this way demonstrate that the distributions of nanowire diameters are defined by those of the nanocluster catalysts. High-resolution TEM shows that the wires are single-crystal zinc blende with a [111] growth direction, and energy-dispersive X-ray analysis (EDAX) confirms that the nanowire composition is stoichiometric GaP.

Recent interest in low-dimensional semiconductor materials has been motivated by the push for miniaturization of electronic and optoelectronic devices and a need to understand the fundamentals of nanoscale chemistry and physics.[5,6] In particular, one-dimensional (1D) systems are exciting from both fundamental and applied viewpoints.[6] Fascinating physical phenomena, such as Luttinger liquid behavior,[7,8] and numerous applications from interconnects to scanning probe microscopies,[9,10] require high-quality, well-defined 1D nanostructures. Experimental progress in the field of 1D nanostructures has often been limited by the ability to create new materials in this size regime with controlled size, structure, and composition.

Early approaches to 1D nanostructure synthesis employed thin film growth and lithographic techniques. In particular, “T-wires” have been fabricated by growing semiconductor quantum wells via molecular beam epitaxy, followed by cleavage and overgrowth on the cleaved surface,[11] while “V-groove” nanowires have been prepared by etching trenches on a surface and then depositing a small amount of material into the resulting grooves.[12] One of the significant limitations of these approaches is that the nanowires are embedded in a substrate, which precludes the assembly of complex 2D and 3D nanostructures. Template approaches have also been used for growing a wide-range of nanowires.[13] These methods can provide good control over the length and diameter of nanowires, although they are limited in that polycrystalline structures are often produced.

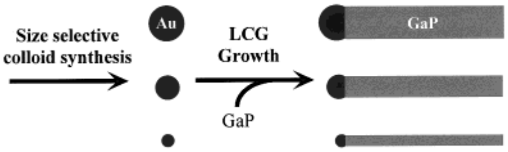

**Figure 1.** Schematic depicting the use of monodisperse gold colloids as catalysts for the growth of well-defined GaP semiconductor nanowires.

Our laboratory has made significant progress toward the development of a general synthetic approach to free-standing single-crystal semiconductor nanowires via the LCG method.[1−4] In LCG, laser ablation of a solid target is used to simultaneously generate nanoscale metal catalyst clusters and reactive semiconductor atoms that produce nanowires via a vapor−liquid−solid growth mechanism.[14] This method has been used to produce a wide range of group IV, III−V, and II−VI nanowires.[1−4,6] We have suggested that the size of the catalyst nanocluster determines the size of the wire during growth, and thus one can envision creating wires with a narrow size distribution by exploiting monodisperse catalyst nanoclusters (Figure 1).[15] Here we utilize nanometer diameter gold colloids to explore this approach.

GaP nanowires were grown by LCG using 8.4, 18.5, and 28.2 nm diameter gold colloids.[16] In these experiments the catalyst nanoclusters are supported on a $SiO_2$ substrate and laser ablation is used to generate the Ga and P reactants from a solid target of GaP. Field emission scanning electron microscopy (FESEM) demonstrates that nanowires with lengths exceeding 10 $\mu$m (Figure 2a) were obtained using all three sizes of catalyst. Examination of the nanowire ends also shows the presence of the nanocluster catalyst (Figure 2a, inset). Control experiments carried out without the Au colloids did not produce nanowires. The FESEM images show that the nanowire diameter distributions are narrower than obtained in experiments without the colloid catalysts, although FESEM is not a good method for quantifying these distributions since small variations in the focal plane can produce significant changes in the observed diameter.

To obtain a quantitative measure of the nanowire diameter distributions produced using the gold colloids, and to better characterize their structure and composition, we used TEM. High resolution TEM shows that the wires are single crystal (Figure 2b), growing in the [111] direction, and EDAX confirms the composition to be stoichiometric GaP (Ga:P 1.00:0.94), within the limits of this technique. Significantly, extensive TEM analysis of nanowire diameters demonstrates the extremely good correla-

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(15) At the time of writing, the authors became aware of a solution-based approach for silicon nanowire synthesis which also exploited one size of colloid for diameter control (Holmes, J. D.; Johnston, K. P.; Doty, C.; Korgel, B. A.; *Science* **2000**, *287*, 1471).

(16) The growth apparatus used in these experiments is similar to that reported.[1] Substrates were made by placing a silicon wafer with 600 nm of thermal oxide (Silicon Sense) into a solution of 95:5 $EtOH:H_2O$ with 0.4% *N*-[3-(Trimethoxysilyl)propyl]-ethylenediamine for 5 min, followed by curing at 100−110 °C for 10 min. Solutions of Au colloids (Ted Pella) were diluted to concentrations of $10^9$−$10^{11}$ particles/mL to minimize aggregation and were deposited on the substrates. Substrates were placed in a quartz tube at the downstream end of the furnace with a solid target of GaP placed 3−4 cm outside of the furnace at the upstream end. The chamber was evacuated to less than 100 mTorr, and then maintained at 250 Torr with an Ar flow of 100 sccm. The furnace was heated to 700 °C and the target was ablated for 10 min with an ArF excimer laser ($\lambda$ = 193 nm, 100 mJ/pulse, 10 Hz). After cooling, the substrates were examined by FESEM (LEO 982). For TEM (JEOL 200CX and 2010) and EDAX analysis, nanowires were deposited onto copper grids after removal from the substrates by sonication in ethanol.

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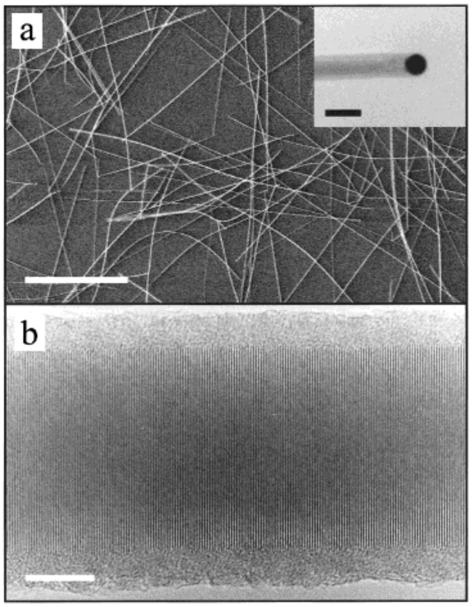

**Figure 2.** (a) FESEM image of nanowires synthesized from 28.2 nm colloids (scale bar is 5 μm). The inset is a TEM image of the end of one of these wires (scale bar is 50 nm). The high contrast feature corresponds to the colloid catalyst at the end of the wire. (b) TEM image of another wire in this sample (scale bar is 10 nm). The [111] lattice planes are resolved, showing that wire growth occurs along this axis, in agreement with earlier work.[1,2] Measurement of the inter-plane spacing gives a lattice constant of 0.54 nm (±0.05 nm) for the wire, in agreement with the bulk value for GaP, 0.5451 nm.

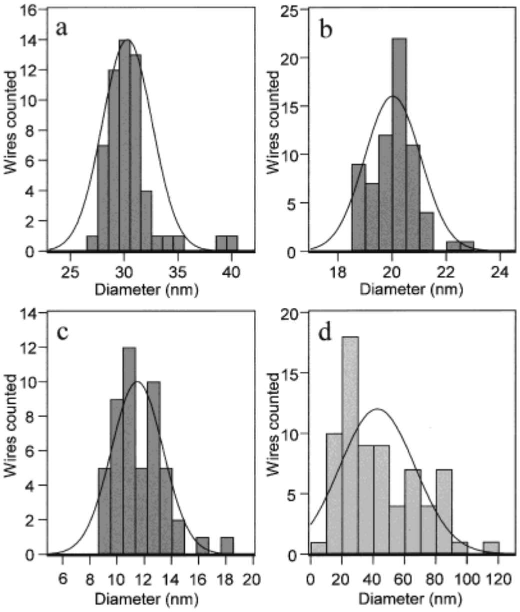

**Figure 3.** Histograms of measured diameters for wires grown from (a) 28.2 nm, (b) 18.5 nm, and (c) 8.4 nm colloids. The solid lines show the wire distributions. (d) Histogram of diameters for wires grown using the previous method without colloids,[2] in which the laser is used to both generate the Au nanoclusters and the GaP reactants. The distribution is very broad (SD = 23.9 nm) and the mean diameter (42.7 nm) greater than those synthesized using the predefined colloid catalyst. In all cases, the reported nanowire diameters correspond to the crystalline cores. The amorphous oxide layers on the surface of all nanowires are relatively uniform from wire-to-wire within the same experiment, but vary from 2 to 6 nm in thickness between syntheses.

tion with the colloid catalyst diameters and dispersion (Figure 3); that is, for wires grown from 28.2 ± 2.6, 18.5 ± 0.9, and 8.4 ± 0.9 nm colloids we observe mean diameters of 30.2 ± 2.3, 20.0 ± 1.0, and 11.4 ± 1.9 nm, respectively. The mean nanowire diameter is generally 1−2 nm larger than that of the colloids. We believe that this increase is due to alloying of the Ga and P reactants with the colloids before nucleation of the nanowire occurs. For the 30 and 20 nm wires (Figs. 3a, b) it is clear that the width of the nanowire distributions mirrors those of the colloid, suggesting that the monodispersity of the wires is limited only by the dispersity of the colloids. For the 10 nm diameter wires (Figure 3c), a small broadening (1 nm) of the wire distribution can be attributed to aggregation of the colloids.[17] The fact that the distribution has peaks separated by ∼2.5 nm suggests that some of the wires grow from aggregates of two colloids, although additional work is required to substantiate this point. In all cases, the distribution of wire diameters is more than an *order of magnitude* narrower than those grown without the use of colloid catalyst (Figure 3d): 43 ± 24 nm.

We believe that this work demonstrates clearly for the first time an ability to exert systematic control over the diameter of semiconductor nanowires for a variety of colloids.[15] Previous attempts to grow nanowires on surfaces with poorly defined catalysts resulted in nanowires with nonuniform diameters greater than 50 nm.[18] Other attempts to control the diameter of nanowires by varying the background carrier gas[19] merely shifted the mean diameter of the wires slightly and yielded much broader distributions of wires than we have achieved with colloid-mediated growth.

In summary, we have demonstrated the controlled synthesis of semiconductor wires with monodisperse diameter distributions. These high-quality, single crystalline wires represent good candidates for both further studies of low-dimensional physics as well as for applications in various fields of nanoscale science and technology. In particular, we believe that the synthesis of controlled diameter samples will greatly facilitate the assembly of these nanoscale building blocks into complex and functional 2D and 3D nanosystems.

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(17) The mean diameter and distribution width increased as more concentrated solutions of the colloid were dispersed onto the substrate.

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