Synthetic Control of the Diameter and Length of Single Crystal Semiconductor Nanowires

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A general synthetic method has been developed to control both the diameter and the length of nanowires during growth. This approach exploits monodisperse nanocluster catalysts to define both the nanowire diameter and the initiation of nanowire elongation during growth by a vapor−liquid−solid mechanism. To demonstrate this new approach, crystalline indium phosphide (InP) nanowires have been synthesized using a laser catalytic growth (LCG) process combined with gold nanocluster catalysts. InP nanowires with nearly monodisperse diameters of 10, 20, and 30 nm were grown from nanocluster catalysts having diameters of 10, 20, and 30 nm, respectively. High-resolution transmission electron microscopy studies show that the InP nanowires prepared in this manner are single crystals with a [111] growth direction. In addition, studies of nanowire growth as a function of growth time have shown that nanowire length is directly proportional to growth time and have enabled the preparation of InP nanowires with narrow length distributions centered at 2, 4, 6, and 9 μm. The new level of synthetic control afforded by our approach should enable better-defined fundamental studies of nanowires and open up new opportunities for the assembly of functional nanodevices.

Introduction

Interest in low-dimensional systems, such as zero-dimensional (0D) nanoclusters and one-dimensional (1D) nanowires, has been sparked by a desire to tune the fundamental optical and electronic properties of materials through rational control of their physical size.[1,2] To realize the potential impact of these materials in nanoscale chemistry and physics, from both fundamental and applied viewpoints, demands materials of well-defined size, structure, and composition. One-dimensional materials,[1] in contrast to 0D nanoclusters,[2] have been relatively unexplored, primarily due to the synthetic challenge of producing high-quality materials of controlled size. The utility of nanowire materials in a myriad applications from devices and interconnects[3,4] for molecular computing to scanning probe microscopy tips[5] emphasizes a definite need for high-quality nanowires.

The importance of "bottom-up" chemical approaches to high-quality, free-standing nanowires cannot be overstated. "T-wires"[6] and "V-groove"[7] wires are both examples of high-quality nanowires produced via a combination of lithographic and epitaxial growth techniques. These approaches are intrinsically limited in that the wires remain embedded in the substrates, precluding assembly into complex devices or new tools. Others have grown nanowires via template approaches,[8] giving rise to nanowires of well-defined diameters and lengths. Nonetheless, these approaches have the drawback that they often produce polycrystalline materials, which are less suitable for both fundamental and applied studies.

Our laboratory has made significant steps toward the development of a general synthetic methodology for semiconductor nanowires via the laser catalytic growth (LCG) method.[9,10] Early experiments utilized the laser ablation of a solid target to generate simultaneously semiconductor reactants and nanocluster catalysts, which produce nanowires via a vapor−liquid−solid (VLS)[11] growth mechanism. This approach has yielded a wide range of group IV, III−V, and II−VI nanowires,[9,10] including control over n- and p-type doping.[4,12] In addition, we recently demonstrated that well-defined gold colloids could be exploited as catalysts for the growth of GaP nanowires with diameter distributions defined by those of the nanocluster catalysts.[13,14] Here, we significantly extend this methodology by demonstrating that nanocluster catalysts can be used to control both the diameter and the length of semiconductor nanowires.

The conceptual ideas underlying diameter- and length-controlled growth of nanowires are illustrated in Figure 1. This approach exploits monodisperse nanocluster catalysts to define both nanowire diameter (Figure 1a) and initiation of nanowire elongation during growth by a vapor−liquid−solid mechanism. By varying the ablation time in LCG, we were able to grow selectively nanowires of a given length (Figure 1b). We report the growth of indium phosphide (InP) nanowires using predefined gold colloids as the nanocluster catalyst but note that the method is applicable to all semiconductor nanowires previously synthesized.[9,10] InP is an intriguing material because of its optoelectronic properties as a direct band gap semiconductor with strong photoluminescence, and thus, controlled diameter and length could open up a number of opportunities for fundamental research and applications.

Experimental Section

InP nanowires were grown using the laser catalytic growth process described previously.[9,10,13] Substrates for nanowire growth were made by functionalizing the surface of a silicon substrate (silicon with 600 nm of thermal oxide, Silicon Sense) for 1 min with a solution of 0.1% poly-L-lysine (Ted Pella). Gold nanocluster solutions (BBI International) were diluted to concentrations of $10^{10}-10^{11}$ particles/mL and were dispersed onto the substrates and then the substrates were quickly (<5 s.) rinsed with water. Atomic force microscopy images of the nanocluster-functionalized surfaces confirmed that the clusters were not aggregated on the surface. These substrates were then placed into a quartz tube at the downstream end of a furnace with a solid target of InP placed about 3−4 cm outside of the
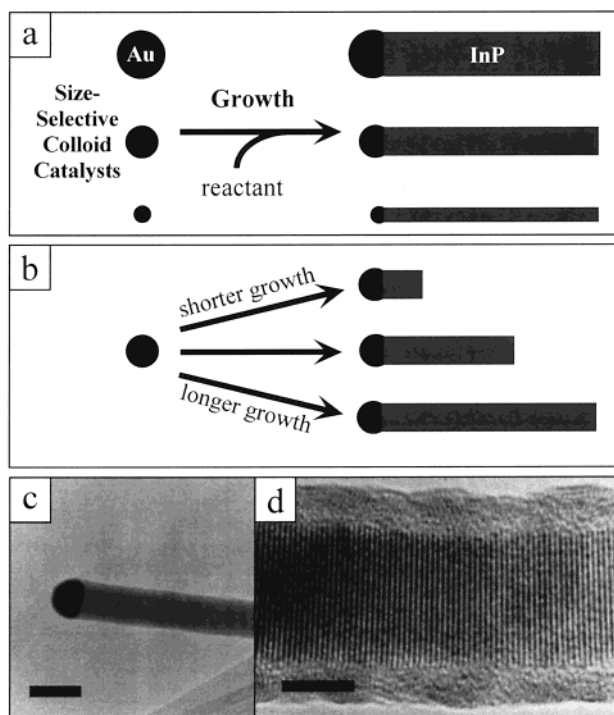
Figure 1. (a) Schematic depicting the use of monodisperse colloid catalysts for the LCG synthesis of diameter-selective InP nanowires. (b) Schematic illustrating the effect of the variation of growth time on nanowire length. (c) TEM image showing the nanocluster catalyst at the end of an InP nanowire grown from a 20 nm Au cluster (scale bar is 50 nm). (d) High-resolution TEM image showing the crystalline core of the InP nanowire grown from a 10 nm colloid (scale bar is 5 nm). The (111) lattice planes resolved perpendicular to the growth axis have an average spacing of 0.59 ± 0.05 nm, which is in good agreement with the bulk value for zinc blende InP of 0.5869 nm.

furnace at the upstream end, where it remains at room temperature during the course of the experiment to avoid thermal evaporation. After evacuating the chamber to less than 100 milliTorr, the chamber was maintained at 200 Torr with a constant flow of 100 standard cubic centimeter per minute (sccm) of Ar. The furnace was heated to 650–700 °C (temperature at the substrate is approximately 500–600 °C), and the InP target was ablated for several minutes with an ArF excimer laser (Lambda Physik, $\lambda = 193$ nm, 100 mJ/pulse, 10 Hz). After cooling the furnace, the samples were examined by field emission scanning electron microscopy (FE-SEM, LEO 982) and were subsequently sonicated in ethanol to remove the wires from the substrates before deposition onto copper grids for transmission electron microscopy (TEM, JEOL 200CX, and JEOL 2010) analysis. Wire diameters were measured using TEM, whereas the lengths were determined from SEM images. For each ablation time, between 80 and 150 wires were measured to assess the distribution of lengths. The composition of individual wires was assessed by energy-dispersive X-ray analysis measurements (EDAX). These measurements confirm that the wires are stoichiometric InP (1.00:1.03), within the resolution of this technique.

Results and Discussion

InP nanowires were grown on substrates containing dispersed Au nanoclusters with diameters of 9.7 ± 1.0, 19.9 ± 3.0, and 30.0 ± 6.0 nm. Figure 1c and 1d shows representative TEM images of a nanocluster catalyst at a nanowire end and a crystalline wire core produced using 20 and 10 nm diameter gold nanoclusters, respectively. The lower resolution image of
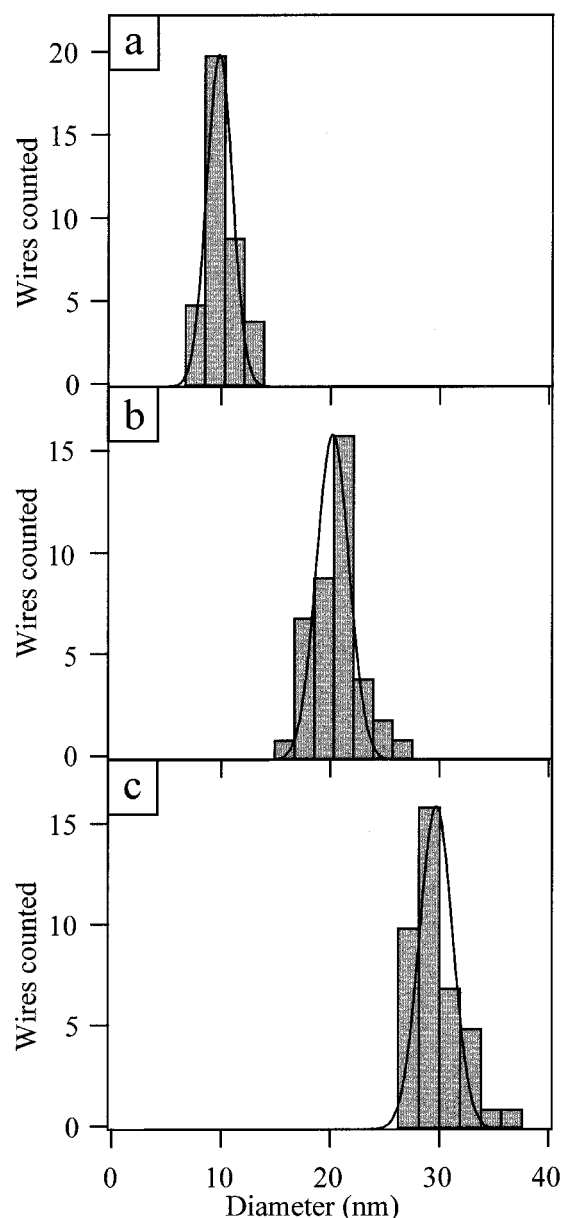
Figure 2. Distributions of wire diameters grown from (a) 9.7 nm, (b) 19.9 nm, and (c) 30.0 nm colloids. The solid lines show a Gaussian fit of the wire distributions. For each set of wires, the diameter distributions are defined by the nearly monodisperse colloid catalyst.

the wire end shows that the catalyst cluster diameter is similar to that of the nanowire product. The well-resolved (111) lattice planes perpendicular to the nanowire axis demonstrate that the wires are crystalline and that growth occurs along the [111] direction. In all cases, the measured wire diameter corresponds to the crystalline core. An amorphous layer of 2–4 nm in thickness is found on all wires and is of relatively constant thickness for all wires in a given experiment. EDAX measurements show that the amorphous layer is an oxide, which is believed to form after removal of the wires from the growth apparatus.[15]

Careful TEM analysis of the InP nanowire diameters obtained following growth from the 9.7 ± 1.0, 19.9 ± 3.0, and 30.0 ± 6.0 nm nanocluster catalysts showed that the nanowires had diameters of 9.8 ± 1.4, 20.2 ± 2.2, and 29.7 ± 2.2 nm (Figure 2), respectively. Significantly, the nanowire diameters (crystalline core) mirror those of the colloid catalyst, whereas the dispersions in the wire diameters are equal to or narrower than
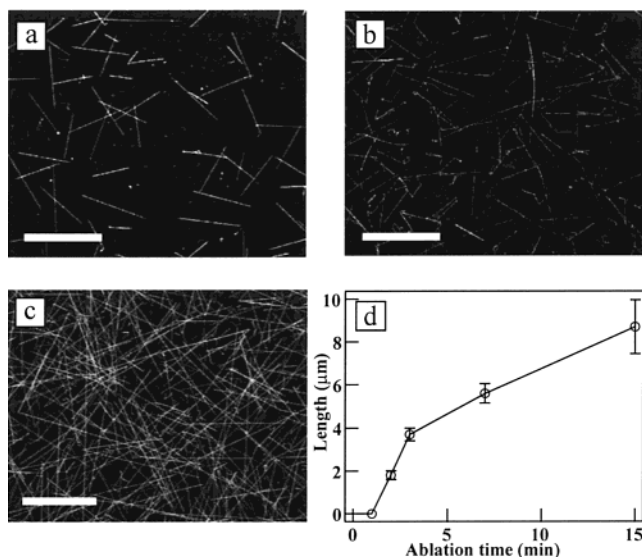
Figure 3. FE-SEM images of nanowires produced after growth times of (a) 3 min, (b) 7 min, and (c) 15 min. All scale bars correspond to 5 μm. (d) Plot showing the relation between growth time and nanowire length.

the dispersion of the Au nanocluster diameters reported by the manufacturer. In addition, our new experiments show more nearly monodisperse samples than those we observed previously for the smallest GaP wires.[13] We attribute this to improvements in the substrate preparation, which has produced well-dispersed Au nanoclusters that do not aggregate during growth. The ability to prepare monodisperse samples of the smallest diameter nanowires will be especially important for fundamental studies investigating quantum effects in these 1D materials. These results attest to the generality of this approach to diameter-controlled synthesis of nanowires via LCG using predefined nanocluster catalysts, and moreover, we note that this approach can be readily extended to diameter-controlled growth using other reactant sources.

To address the issue of length control, we have carried out nanowire synthesis for a series of growth times using 20 nm gold colloids. FE-SEM images of the nanowire products produced for 3, 7, and 15 min growth times are shown in Figure 3a−c. Inspection of these FE-SEM images indicates a strong correlation of growth time with nanowire length. To assess quantitatively the relationship between nanowire lengths and growth times, we have systematically analyzed a large number of samples. Specifically, quantitative analysis of the wire lengths as a function of 2, 3, 7, and 15 min growth times showed wire lengths of 1.8 ± 0.2, 3.7 ± 0.3, 5.6 ± 0.5, and 8.7 ± 1.3 μm. Figure 3d depicts clearly the systematic increase in nanowire length with growth time, and also shows that the distribution of lengths is quite small at short growth times.

Studies of the very early stages of growth have also shown that the nucleation of the wires occurs after ca. 1−2 min. This initiation period is due to the finite period of time required to saturate the gold nanocluster with the InP reactants and achieve nucleation. After nucleation, nanowire elongation proceeds at a fairly constant rate, giving rise to wires of a well-defined length and narrow distributions,[16] thereby illustrating our ability to

systematically vary nanowire length by utilizing colloid-mediated growth. This systematic control of the nanowire length represents a second significant improvement in our ability to synthesize wires of a desired, narrowly distributed size.

In conclusion, we have shown that well-defined nanocluster catalysts can be used to define both the nanowire diameter and the initiation of nanowire elongation and hence nanowire length during the growth of InP materials by the LCG method. Because the LCG methodology and VLS growth mechanism provide a general approach to the controlled synthesis of compound semiconductor nanowires, this work represents a wide-ranging approach to the synthesis of nanowire samples with monodisperse diameters and lengths. Our ability to exert a high degree of control over both the diameter and the length of nanowires will also facilitate the study of size-dependent electrical transport, optical properties and optoelectronic phenomena in these nanostructures. Last, we believe that the ability to exert this new level of synthetic control over nanowires will open up exciting opportunities for the hierarchical organization of nanowires that are essential for building complex functional nanodevices.[4,17]

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(16) The standard deviation of the length distributions increases over time. We believe that this may be due to factors such as turbulence in the reactor flows and inhomogeneous reactant concentrations as the nanowire density increases. Further studies will be required, however, to clarify and substantiate this point.

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