

## Diameter-controlled synthesis of single-crystal silicon nanowires

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Monodisperse silicon nanowires were synthesized by exploiting well-defined gold nanoclusters as catalysts for one-dimensional growth via a vapor–liquid–solid mechanism. Transmission electron microscopy studies of the materials grown from 5, 10, 20, and 30 nm nanocluster catalysts showed that the nanowires had mean diameters of 6, 12, 20, and 31 nm, respectively, and were thus well defined by the nanocluster sizes. High-resolution transmission electron microscopy demonstrated that the nanowires have single-crystal silicon cores sheathed with 1–3 nm of amorphous oxide and that the cores remain highly crystalline for diameters as small as 2 nm. © 2001 American Institute of Physics. [DOI: 10.1063/1.1363692]

The synthesis and characterization of silicon nanowires (SiNWs) have recently attracted great attention.<sup>1–5</sup> SiNWs have been demonstrated to function as simple field-effect transistors,<sup>6,7</sup> and more recently, we have shown that specifically doped *p*- and *n*-type SiNWs can be assembled to form *p*–*n* junctions, bipolar transistors, and complementary inverters.<sup>8</sup> These results thus suggest that SiNWs could be used as critical components for nanoelectronic devices, acting as both functional units and interconnects.

The electrical and optical properties of SiNWs are, however, strongly size dependent. To explore the effects of quantum confinement on electrical and optical properties, high-quality SiNWs with well-defined and monodisperse diameters are necessary. Previously, variations of ambient gases<sup>4</sup> and ambient pressure<sup>5</sup> have been studied in attempts to modify the diameter of SiNWs. These variations led to shifts in the mean wire diameters, but the SiNWs produced in these studies exhibited broad diameter distributions. More recently, the synthesis of 4–5-nm-diam SiNWs in supercritical hexane was reported.<sup>3</sup> The nanowires produced in this way had small diameter distributions, although undesirable impurities such as gold (Au) and carbon were detected.

Our group has previously demonstrated the general synthesis of high-quality single-crystal nanowires (NWs) of group IV, III–V, and II–VI semiconductors<sup>1,9–11</sup> via a vapor–liquid–solid (VLS) growth mechanism, in which metal nanoclusters mediate (i.e., function as catalysts) the NW growth. In this approach, the size of the metal catalysts should determine the diameter of the NWs, implying that NWs with a narrow size distribution could be obtained by exploiting well-defined catalysts [Fig. 1(a)]. This idea was verified recently for the controlled diameter growth of GaP nanowires by laser ablation.<sup>12</sup> Here, we demonstrate the synthesis of high-quality single-crystal SiNWs with well-controlled diameters by using well-defined Au nanocluster catalysts and silane (SiH<sub>4</sub>) as the vapor-phase reactant.

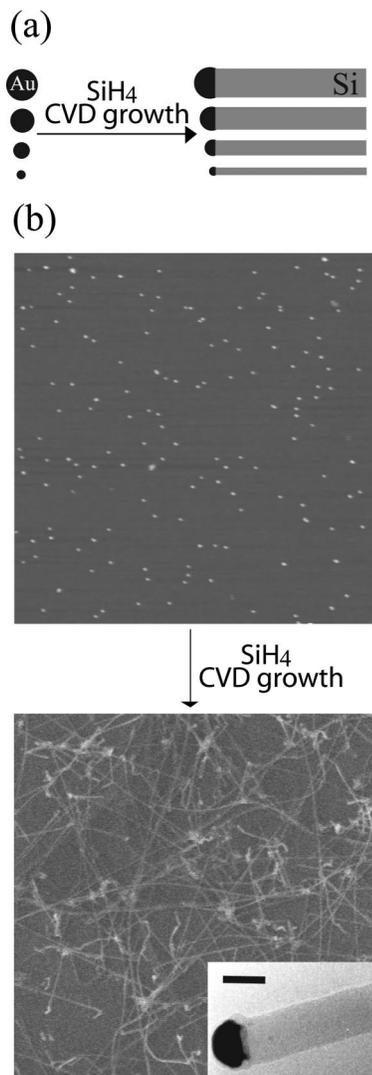


FIG. 1. (a) Schematic illustrating size-controlled synthesis of SiNWs from Au nanoclusters. (b) AFM image of 10 nm Au nanoclusters dispersed on the substrate (top). FESEM image of SiNWs grown from the 10 nm nanoclusters (bottom). The sides of both images are 4  $\mu$ m. The inset in the bottom image is a TEM micrograph of a 20.6-nm-diam SiNW with a Au catalyst at the end. The scale bar is 20 nm.

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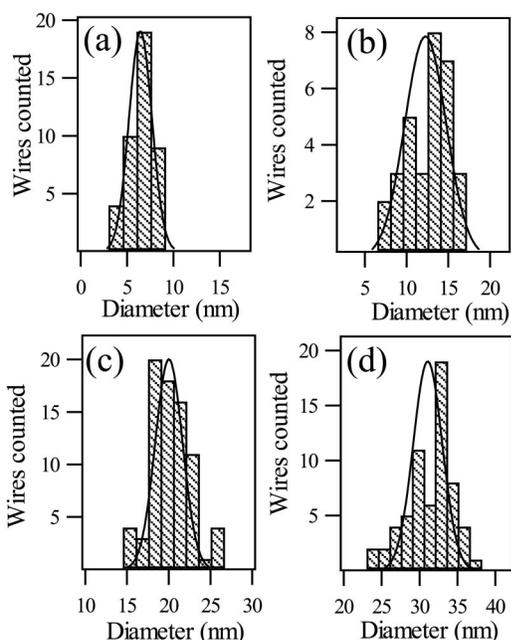


FIG. 2. Histograms of SiNW diameters grown from 5-, 10-, 20-, and 30-nm-diam Au nanoclusters. The smooth curves show a Gaussian fit of the wire distributions. The calculated NW diameters include the oxide.

The growth apparatus is similar to that previously described.<sup>1</sup> Growth substrates were prepared by depositing 0.1% poly-*L*-lysine (Ted Pella) on oxidized silicon wafers, and then nominally 5, 10, 20, and 30 nm Au nanoclusters (Ted Pella, diluted to  $10^{11}$ – $10^{12}$  particles/ml). The negatively charged nanoclusters stick to the positively charged poly-*L*-lysine. Atomic-force microscopy (AFM) was used to verify that the nanoclusters were well dispersed on the substrates [Fig. 1(b)]. The substrates prepared in this way were cleaned in an oxygen plasma (100 W, 0.7 Torr, and 250 sccm  $O_2$  flow rate) for 5 min, and then placed in a quartz reactor at the downstream end of the furnace. The reactor was evacuated to less than 100 mTorr, heated to  $\sim 440^\circ C$  under Ar flow, and then SiNWs were grown for 5–10 min with a 10–80 sccm flow of  $SiH_4$  (10% in He).

Figure 1(b) shows a field-emission scanning electron microscopy (FESEM) image of the SiNWs produced from 10-nm-diam Au nanoclusters. The NW density is comparable to the nanocluster density, indicating that SiNW nucleation is dominated by these clusters. Qualitatively, the FESEM images show that the SiNWs grown from Au nanoclusters are nearly monodisperse with diameters determined by the nanoclusters. Transmission electron microscopy (TEM) images [e.g., Fig. 1(b), bottom inset] show that the Au particles at the NW ends are similar to the NW diameters, and thus support this suggestion. The smooth structure of our SiNWs indicates that these NWs have fewer defects than those grown by  $SiO_2$ -mediated or Si thermal evaporation methods.<sup>4,5</sup> The low density of defects is confirmed by high-resolution TEM (HRTEM) (see below). The gradual bending of the NWs observed over  $\sim 10\text{-}\mu m$ -length scale is due to elastic strains on these very small diameter wires.

To quantify the diameter distributions of SiNWs grown from different diameter nanocluster catalysts, we have carried out extensive TEM analysis. Histograms of the NW diameters obtained from different diameter nanoclusters are

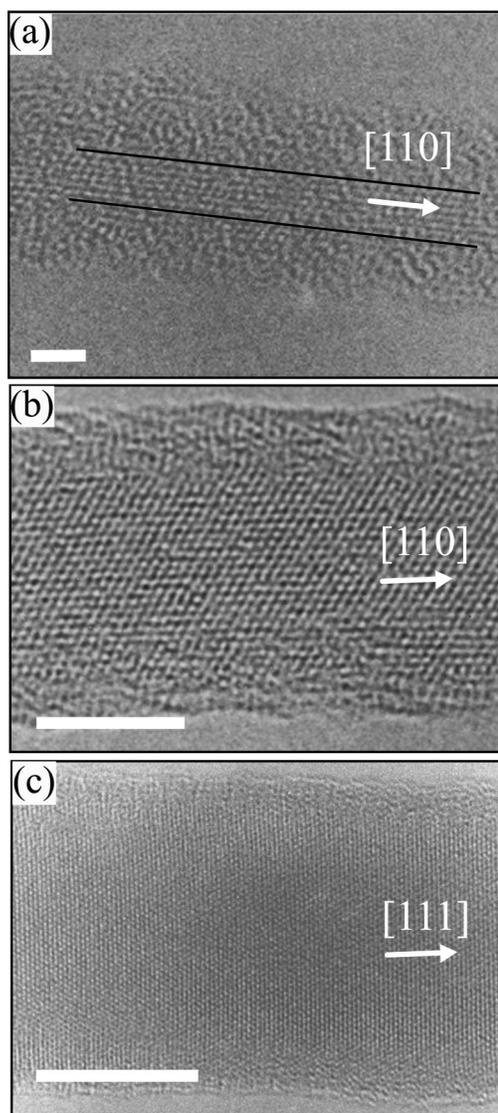


FIG. 3. HRTEM images of (a) 6.7-nm-, (b) 10.7-nm-, and (c) 20.6-nm-diam NWs grown from 5, 10, and 20 nm catalysts, respectively. The scale bars are 2, 5, and 10 nm, respectively. In (a), the black lines indicate the crystalline Si core.

plotted in Fig. 2. For SiNWs grown from 5 nm ( $4.9 \pm 1.0$  nm), 10 nm ( $9.7 \pm 1.5$  nm), 20 nm ( $19.8 \pm 2.0$  nm), and 30 nm ( $30.0 \pm 3.0$  nm) Au nanoclusters, the average NW diameters were  $6.4 \pm 1.2$ ,  $12.3 \pm 2.5$ ,  $20 \pm 2.3$ , and  $31.1 \pm 2.7$  nm, respectively. Significantly, the dispersity of the SiNW diameters mirrors that of Au catalysts, suggesting that the dispersity of the SiNWs is limited only by the dispersity of Au nanocluster catalysts. The NW diameters were on average 1–2 nm larger than the catalyst sizes. This observation is consistent with the formation of a Si/Au alloy prior to the nucleation of NW growth. In addition, postgrowth oxidation of the SiNWs upon exposure to air could also increase the observed wire diameters. Overall, these results testify to the validity of our size-controlled growth approach, and also demonstrate that it is possible to produce monodisperse SiNWs with specific core diameters ranging from only 2 to more than 30 nm.

We have also examined the structures of these SiNW samples in more detail with HRTEM to search for size-dependent growth behavior. HRTEM images (Fig. 3) of 6.7-,

10.7-, and 20.6-nm-diam NWs show that the NWs have single-crystalline cores sheathed with a layer of 1–3 nm amorphous SiO<sub>x</sub>. The SiNWs remain highly crystalline even for core diameters as small as 2 nm [Fig. 3(a)], which is a small diameter for free-standing SiNWs. Nanowire growth directions of [110] [Figs. 3(a) and 3(b)] and [111] [Fig. 3(c)] have been observed. Significantly, our preliminary analysis suggests that the smallest SiNWs prefer growth along the [110] direction, while larger NWs are almost exclusively [111]. We believe that these preferences may reflect competing catalyst/SiNW interface and SiNW surface energetics, although additional analysis will be needed to define this point in the future.

In conclusion, monodisperse SiNWs were synthesized by exploiting well-defined Au nanoclusters as catalysts for one-dimensional growth via a VLS mechanism. The SiNWs grown from 5, 10, 20, and 30 nm nanocluster catalysts had mean diameters of 6, 12, 20, and 31 nm, respectively, and the diameter distributions of the SiNWs mirror those of catalysts. HRTEM demonstrates that these SiNWs have single-crystal silicon cores sheathed with 1–3 nm of amorphous oxide, and that the cores remain crystalline for diameters as small as 2 nm. We believe that these high-quality single-crystal SiNWs with well-defined and predictable diameters will provide substantial opportunities for the exploration of

the effects of quantum confinement on electrical and optical properties of one-dimensional silicon structures, and for the assembly of nanoelectronic devices from NW building blocks.

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