Controlled Growth and Structures of Molecular-Scale Silicon Nanowires

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ABSTRACT

Single-crystal silicon nanowires with diameters approaching molecular dimensions were synthesized using gold nanocluster-catalyzed 1D growth. High-resolution transmission electron microscopy studies show that silicon nanowires grown with silane reactant in hydrogen are single crystal with little or no visible amorphous oxide down to diameters as small as 3 nm. Structural characterization of a large number of samples shows that the smallest-diameter nanowires grow primarily along the $\langle 110 \rangle$ direction, whereas larger nanowires grow along the $\langle 111 \rangle$ direction. In addition, cross-sectional transmission electron microscopy was used to address the importance of surface energetics in determining the growth direction of the smallest nanowires. The ability to prepare well-defined molecular-scale single-crystal silicon nanowires opens up new opportunities for both fundamental studies and nanodevice applications.

One-dimensional nanostructures such as semiconductor nanowires (NWs) are attractive building blocks for the assembly of nanoelectronic and nanophotonic systems because they can function both as nanoscale devices and interconnects.[1] Silicon nanowires (SiNWs) represent a particularly attractive class of building blocks for nanoelectronics because their diameter and electronic properties can be controlled during synthesis in a predictable manner.[2−4] The ability to control the electronic properties has been utilized for the reproducible assembly of field-effect transistors (FETs),[4−6] logic gates,[7] and sensors.[8] In addition, recent studies have suggested that SiNWs FETs can exhibit transport characteristics that are comparable to or exceed the best planar devices fabricated by top-down approaches.[6] These latter results are intriguing because they indicate that these SiNW FETs may offer advantages compared to lithographically patterned silicon nanostructures. To understand these results will require better control of diameter and surface properties, including reduction of the SiNW diameters to the molecular scale, where it may be possible to achieve true 1D behavior.[9,10]

Previous studies have demonstrated that the synthesis of semiconductor NWs with small diameter distributions can be achieved using well-defined nanoclusters as catalysts in a vapor−liquid−solid (VLS) growth process.[1,3,11] Solution-phase synthesis of SiNWs has also been shown using gold nanocluster catalysts dispersed in supercritical hexane.[12] The SiNWs produced in this way show excellent crystallinity, although the surfaces may be coated by hydrocarbon.[12] SiNWs also have been produced by an "oxide-assisted" method; however, this approach generally yields a broad diameter distribution, bulk defects, and a thick surface oxide layer.[13] Here we describe the controlled growth of single-crystal SiNWs with diameters approaching molecular dimensions. High-resolution transmission electron microscopy (HRTEM) studies show that silicon NWs grown with silane reactant in hydrogen are single crystals with little or no visible amorphous oxide down to diameters as small as 3 nm. Structural characterization of a large number of samples shows that the NWs exhibit narrow diameter distributions and that the smallest-diameter NWs grow primarily along the $\langle 110 \rangle$ direction versus the $\langle 111 \rangle$ direction in larger NWs. In addition, cross-sectional transmission electron microscopy was used to address the importance of surface energetics in determining the growth direction of the smallest NWs.

SiNWs were synthesized by chemical vapor deposition (CVD) using gold nanoclusters as catalysts and silane (SiH_4) as a vapor-phase reactant. The growth procedure is similar to that described previously except that H_2 was used as the carrier gas.[3,14] Representative HRTEM images of SiNWs grown using 10-, 5-, and 2-nm average diameter gold nanocluster catalysts show that the NWs are single crystals (Figure 1). The reciprocal lattice peaks, which were obtained from 2D Fourier transforms of the lattice-resolved images (insets, Figure 1a−c), show that the growth axes are $\langle 112 \rangle$,

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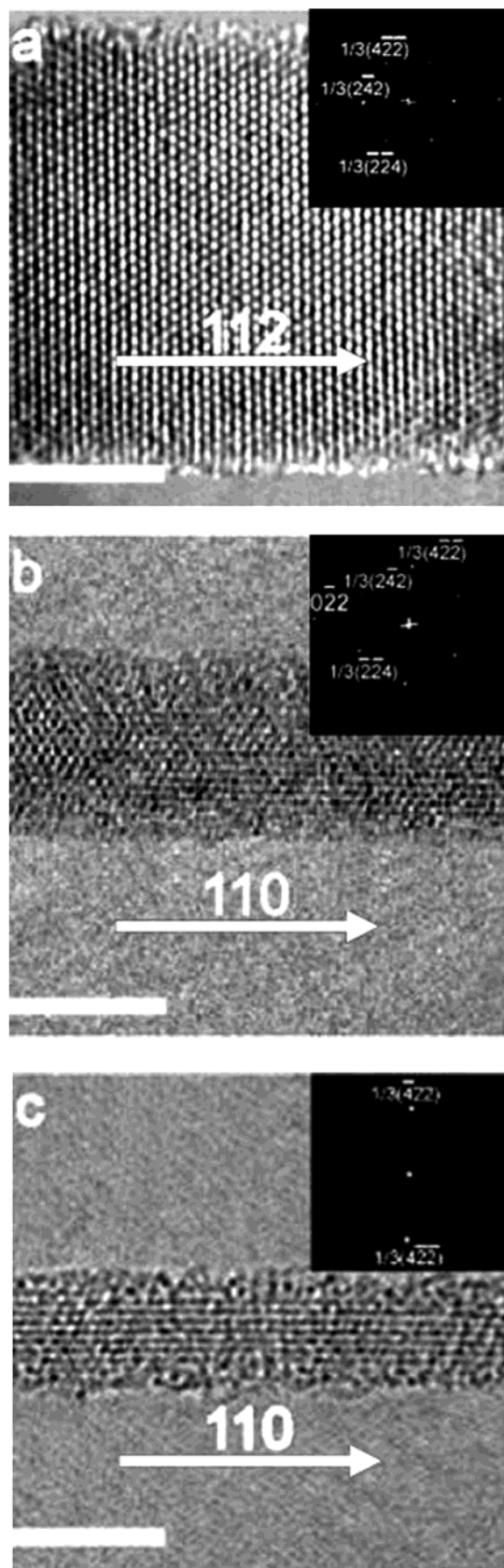§ Division of Engineering and Applied Sciences.

Figure 1. HRTEM images of SiNWs with diameters of (a) 13.2, (b) 5.7, and (c) 3.5 nm. SiNWs were grown from 10-, 5-, and 2-nm gold nanoclusters catalysts, respectively. The scale bar is 5 nm in each panel. The NW growth axes are indicated by white arrows.
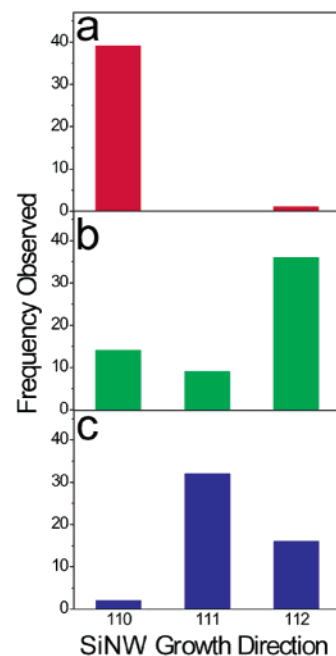

Figure 2. Histograms of the growth directions for SiNWs with diameters from (a) 3 to 10 nm, (b) 10 to 20 nm, and (c) 20 to 30 nm.

⟨110⟩, and ⟨110⟩ for the three NWs. The observed fractional $^1/_3\{422\}$ reflections arise as a result of the finite thickness of the SiNWs.[15]

In addition, the molecular-scale SiNWs synthesized by our approach have little or no visible amorphous oxide down to diameters as small as 3 nm, in contrast to previous work where typically at least 1−3 nm of an amorphous oxide layer was observed.[3,13] We believe that the use of H_2 as the carrier gas passivates the surface in a manner similar to that observed in thin-film growth.[16] Passivation of the SiNW growth surface can stabilize this interface and thereby reduce roughening and is also important for the subsequent elaboration of NW structures by, for example, the growth of Ge[15] and high-dielectric-constant oxide[17,18] shells for high-performance FETs.

The growth axes of a large number of the SiNWs were analyzed as a function of diameter using HRTEM (Figure 2). For diameters between 3 and 10 nm, 95% of the SiNWs grew along the ⟨110⟩ direction; for diameters between 10 and 20 nm, 61% of the SiNWs grew along the ⟨112⟩ direction; and for diameters between 20 and 30 nm, 64% of the NWs grew along the ⟨111⟩ direction. These results demonstrate a clear preference for growth along the ⟨110⟩ direction in the smallest SiNWs and along the ⟨111⟩ direction in larger SiNWs.

The observed preferences for growth directions can be understood in terms of the liquid catalyst alloy/solid SiNW interfacial energy and the SiNW surface energy. Extensive studies of VLS growth of micrometer-scale silicon whiskers have shown that the growth is primarily along the ⟨111⟩ direction. In these cases, the growth axis is believed to be determined by the formation of a single lowest-free-energy solid−liquid interface that is parallel to a single (111) plane.[19]
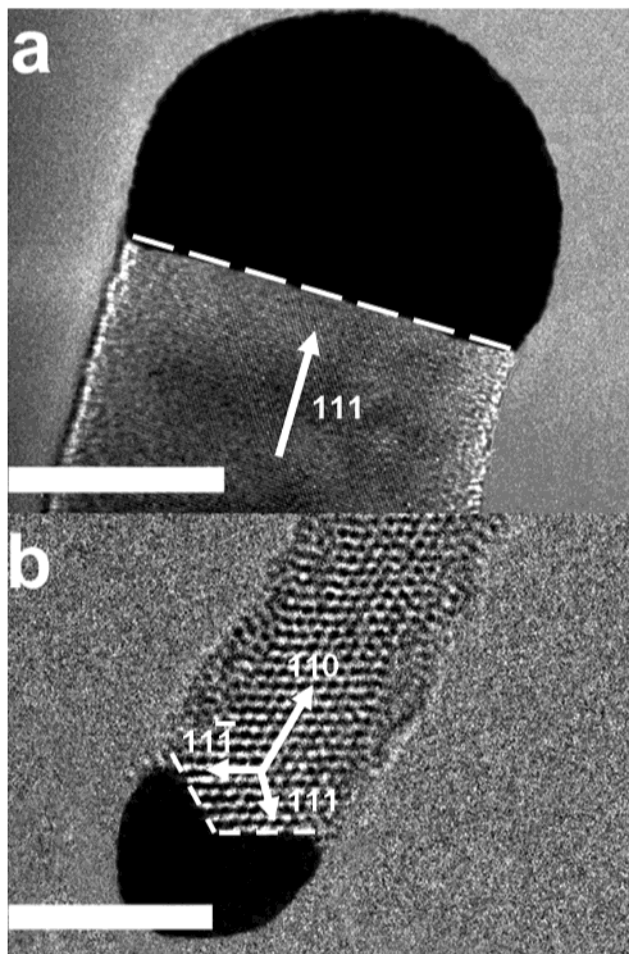
Figure 3. (a) HRTEM image of the catalyst alloy/NW interface of a SiNW with a ⟨111⟩ growth axis. Scale bar, 20 nm. (b) HRTEM image of a catalyst alloy/NW interface of a SiNW with a ⟨110⟩ growth axis. Scale bar, 5 nm.

In our studies of SiNW growth, we observe that an increasing fraction of SiNWs grow along the ⟨111⟩ direction with increasing NW diameter and that for SiNW growing along the ⟨111⟩ direction there is a single catalyst−NW interface that is parallel to the (111) planes (Figure 3a).

The observed growth along the ⟨110⟩ direction in the smallest SiNWs suggests an important role for surface energetics. Indeed, consideration of the structure of an NW with a ⟨110⟩ growth axis suggests that it should be possible to terminate the solid/vacuum interfaces parallel to the axis with the lowest-free-energy (111) and (100) planes.[20] This raises interesting issues regarding the liquid/solid interface during growth and the possible faceting of the NW driven by surface energetics. Significantly, high-resolution imaging of the catalyst/SiNW interface in the smallest NWs shows a well-defined V-shaped morphology (Figure 3b). Crystallographic analysis shows that the interface consists of two {111} planes, whereby the ⟨111⟩ and ⟨11$\bar{1}$⟩ directions combine to yield a growth axis of ⟨110⟩. These results indicate that the liquid/solid (111) interface remains the lowest-energy interface in the smallest NWs; that is, ⟨110⟩ growth does not arise from the formation of a liquid/solid (110) interface. We suggest that a single (111) plane forms

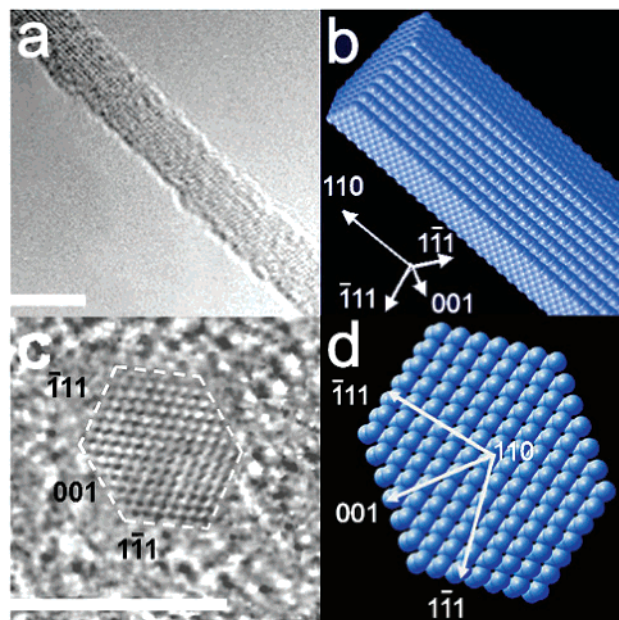**Figure 4.** (a) TEM images of 3.8-nm SiNWs grown along the ⟨110⟩ direction, (c) HRTEM cross-sectional image, and equilibrium shapes for the (b) NW and the (d) NW cross sections predicted by Wulff construction. The scale bars are 5 nm. SiNWs dispersed in epoxy were sectioned with a microtome to slices ca. 50 nm thick and were then transferred to copper TEM grids.

during initial nucleation but as the axial elongation proceeds surface energetics may drive the nucleation of a second (111) plane to enable growth along the ⟨110⟩ direction, which yields the lowest-energy solid/vacuum interfaces. Growth along the ⟨112⟩ direction, which is observed for a substantial fraction of intermediate-diameter SiNWs, has been addressed in recent studies examining the relationships between (112) and (111) planes.[21] Because the (112) plane is a stepped plane between the (111) and (110) planes, we suggest that the ⟨112⟩ direction is a "transitional" direction between the ⟨111⟩ and ⟨110⟩ growth directions.

To address these issues further for molecular-scale SiNWs that grow along the ⟨110⟩ direction, we have recorded cross-sectional HRTEM images (Figure 4). A cross sectional image of a 3.8-nm SiNW with a ⟨110⟩ growth axis reveals that the NW has a hexagonal cross section with well-developed facets. An analysis of the lattice-resolved image shows that these facets correspond to the low-free-energy (111) and (100) planes, which is consistent with the equilibrium shape (Figure 4d) predicted by a Wulff construction.[20] The d spacings measured from the Fourier transform of the cross-sectional image, 3.103 Å for the (111) plane and 2.655 Å for the (200) plane, are within 2% of the expected values. Evidence for faceted structures has also been reported in recent scanning tunneling microscopy (STM) studies of small HF-etched SiNWs,[22] although our cross-sectional HRTEM analysis provides a much more detailed view of this structure in molecular-scale SiNWs.[23]

Last, we have statistically analyzed SiNW diameters produced from different-sized gold nanoclusters. Statistical results based on HRTEM data show that SiNWs grown from

10 (9.7 ± 1.5), 5 (4.9 ± 0.7), and 2 nm (3.3 ± 1 nm) gold nanoclusters have average diameters of 13.2 ± 1.7, 5.9 ± 1.1, and 4.6 ± 1.2 nm, respectively. These results demonstrate good control of the NW diameter, although the diameter is systematically larger than the starting nanocluster size. This increase in NW diameter can be attributed to the supersaturation of silicon in gold nanoclusters during the formation of the liquid nanodroplet prior to nucleation during VLS growth, a phenomena observed previously during in-situ observations of the growth of germanium NWs.[24] Estimates based on the Si−Au phase diagram[25] show that 3.3- and 4.9-nm gold nanoclusters at 435 °C should yield SiNWs with diameters of 3.6 and 5.4 nm, respectively, at the saturation point (22.6% of silicon in a Si−Au alloy droplet); if the supersaturation reaches 50% in the Si−Au alloy nanodroplets, then the SiNW diameters will be 4.3 and 6.3 nm, respectively. This analysis suggests that with decreasing nanocluster size the barrier to nucleation may increase and thus result in greater supersaturation and corresponding NW diameter, although future studies will be required to define unambiguously this point as well as the lower NW diameter limits that can be achieved.[26]

In summary, we have demonstrated the controlled growth of molecular-scale SiNWs with a small diameter distribution. HRTEM images show that the NWs grown with H_2 carrier gas are single crystals with little or no visible amorphous oxide down to diameters as small as 3 nm. The growth direction has a strong diameter dependence, with the smallest-diameter NWs growing primarily along ⟨110⟩ and the larger NWs growing along ⟨111⟩. TEM imaging of the catalyst/NW interface and cross-sectional TEM and modeling studies have provided new insight into the role of surface energetics in determining growth directions and reveal that molecular-scale SiNWs have well-developed facets. The ability to prepare well-defined molecular-scale single-crystal SiNWs should open up new opportunities for fundamental transport studies and nanodevice applications.

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