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Transmission electron microscopy study of Si nanowires

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Microstructures of Si nanowires (SiNW's) synthesized using laser ablation were investigated by transmission electron microscopy. The SiNW's have a high density of structural defects, which may play an important role in the formation of SiNW's and in the determination of the morphology of the nanowires. A model for the growth mechanism of the SiNW's was discussed on the basis of the observation. © *1998 American Institute of Physics.* [S0003-6951(98)00527-0]

The successful synthesis of Si nanowires (SiNW's)[1,2] by laser ablation has stimulated intensive interest in this peculiar one-dimensional nanostructured material, which may have physical properties different from Si,[3,4] Ge,[5,6] and GaAs (Refs. 7 and 8) whiskers with diameters ranging from microns to millimeters. The new nanowires may not only provide opportunities for study of new physical phenomena related to materials of reduced dimensions, but may also facilitate future nanoscale device applications. In approaching this goal, one has to understand the growth mechanism and the structural nature of the nanowires. To date, there has been no detailed study of the structure and growth mechanism of the SiNW's to our knowledge. In this letter, we report on the transmission electron microscope (TEM) observation of the microstructure of SiNW's, and propose a growth model based upon these experimental observations.

The SiNW's were synthesized by the same oven-laser ablation method used for BN nanotubes,[9] and the experimental details of the synthesis were described in our previous work.[1] Bulk quantity of SiNW's is perfectly reproducible. A small piece of the fresh-made product was placed on a Cu supporting grid destined for immediate TEM examination. Conventional TEM analysis was performed using a Philips CM-12 electron microscope. High-resolution electron microscopy (HREM) was conducted using a JEOL-2010 high-resolution electron microscope operating at 200 kV.

Figure 1 is a typical TEM micrograph showing the morphology of the extremely pure SiNW's with uniform distribution of diameters. The average diameter of the SiNW's is about 15 nm and the length varies from a few tens to hundreds of micrometers. The selected-area electron diffraction pattern taken from the SiNW's is shown in the inset on the upper left of the micrograph, which is a typical ring pattern for the bulk silicon.

The HREM images in Fig. 2 show representative structural features of two individual SiNW's with a high density of defects. The incident electron beam is parallel to the [110] zone axis. From these images, one can easily see that a thin amorphous silicon oxide layer with about 2 nm in thickness is always visible on the surface of the SiNW's. In Fig. 2(a), microtwins and stacking faults are visible in a single SiNW with about 10 nm in diameter, and most of the twins are of the $\Sigma 3$ type. Fivefold twins and a zigzag-shaped high order-twin boundary are visible as shown, for example, in the areas marked by letters ''A'' and ''B,'' respectively. The five invariant sectors are related by a common [110] axis around ''A.'' It is worth noting that the nanowire grows along one sector of multiply twinned particles, which can be traced back to the role of the twin quintuplets as the nucleation site of the growing planes at the early stage of SiNW's growth. Accordingly, the center of the twin quintuplet marked by ''A'' can be regarded as a nucleation site center. By analogy, high-order twin boundaries ($\Sigma 9$, $\Sigma 27$, $\Sigma 81$) around ''B'' also provide a clue to understanding the nucleation and growth of the SiNW's. It is simply because the higher-order twin boundaries are the loci of the intersection points of the growing planes on two adjacent twins and serve as an indicator for the local crystal growth direction. The central nucleation site for the growing planes in many cases can be traced back to a quintuplet twin point. Figure 2(b) shows a HREM image

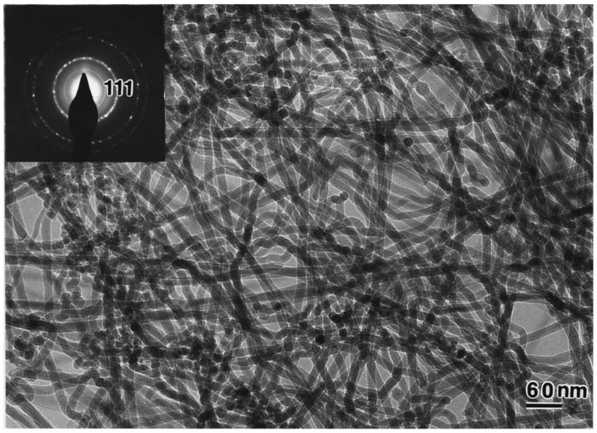

FIG. 1. A typical TEM image showing the general view of morphology of the SiNW's.

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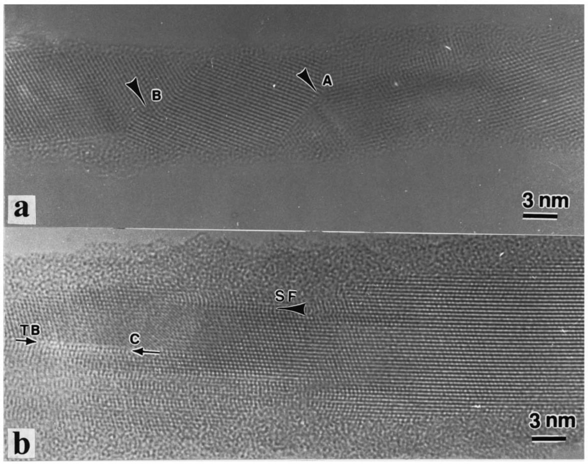

FIG. 2. HREM images of two individual SiNW's revealing abundance of fivefold twins and high-order grain boundaries (a), as well as stacking faults (b).

of a {111} intrinsic stacking fault (labeled ''SF'') in another SiNW. The presence of a high density of planar defects on {111} planes in SiNW's can be attributed to the relative ease of formation of stacking faults on the {111} planes in the silicon structure.

Figure 3 shows some typical morphologies and corresponding HREM images of the SiNW's. For the straight SiNW's [indicated by the arrowheads in the inset of Fig. 3(a)], the growth plane is one of the {111} planes and the fast growth direction is along the [112] axis of the SiNW's. There are also many curved SiNW's with kinks indicated by arrowheads as shown in the inset of Fig. 3(b). From the corresponding HREM image in Fig. 3(b), it is clearly visible that such a kink is normally related to the existence of a twin. In highly curved parts of SiNW's, microtwins are also observed, as shown in Fig. 3(c). All of these results reveal, again, that the morphology of the SiNW's is closely related to the microtwins. Further, it can be concluded that various morphologies of the SiNW's can be consistently explained on the basis of the role of the planar defects during the SiNW's formation. It is interesting to note that the curvature of the SiNW's is dependent on the twinning, while that of carbon nanotubes depends on pentagon–heptagon pairs.

As discussed above, microtwins, stacking faults, and low-angle grain boundaries were found closely related to the formation and the morphology of the SiNW's. In submicron Si particles with a diameter around 200 nm synthesized by the arc-discharge gas evaporation method,[10] multiple twins and stacking faults frequently occurred in the center of the spherical Si particles. In the growth of germanium, the importance of twins has been utilized to describe the growth of germanium dendrites from a melt.[11] Hamilton and Seidensticker[12] utilized the $\Sigma 3$ twin boundaries reentrant angle 141° model to explain the preferred crystal growth site. Under equilibrium growth conditions, silicon atoms attached to a free surface of the growing crystals are relatively stable and can stay in position, thus forming a preferred site for the formation of a new {111} plane. In the course of the SiNW's growth by laser ablation, however, the growth condition is nonequilibrium, and it is likely that Si atoms positioning themselves in a reentrant angle site will be more stable. When a new plane forms at the reentrant site, it can grow rapidly because there are stable positions at the step site of the propagating plane. Therefore, an abundance of planar defects may play an important role in the SiNW's formation, and particularly the triple, quadruple, and quintuplet junction points of the microtwin variants can serve as the center of nucleation of the SiNW's.

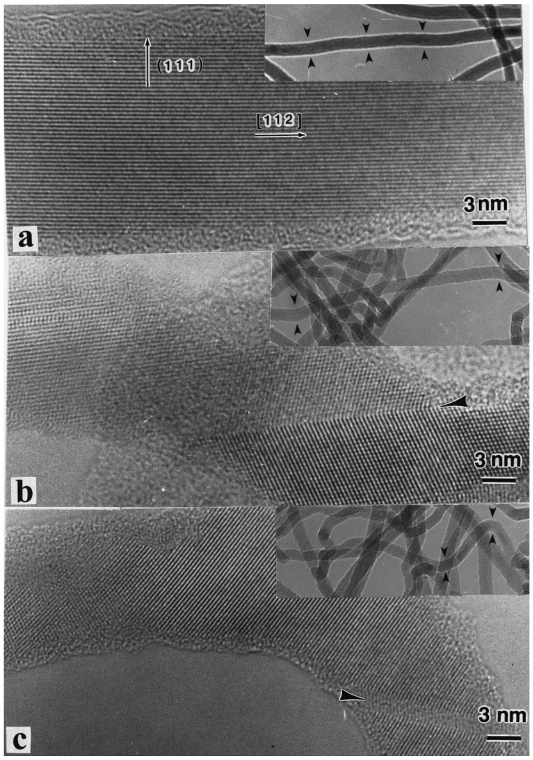

FIG. 3. HREM images of microstructure details which are related to different morphologies represented in the insets: (a) a straight SiNW whose axis is parallel to the [112] direction; (b) a SiNW with kink; and (c) a curved SiNW.

Synthesis of silicon and germanium nanowires were also reported[2] recently by another group using an approach similar to ours, but there are some dissimilarities in location of the deposit, purity, morphology, growth direction, and defects between the two studies. In contrast to our results, their product consists of silicon nanowires all terminated at one end with larger nanoparticles, and was much less pure (only about 50% is SiNW's, and the remaining product is composed of Si, Fe, and O) compared to ours (about 99% of SiNW's). In their analysis, evidence of twins was found in germanium nanowires, but not in SiNW's, and the general growth direction was found along the ⟨111⟩ direction, so the well known vapor–liquid–solid[13] model was used to explain the SiNW's growth. Based on the HREM observations of various structure defects discussed above, however, our study emphasized the important role that these defects may play in the formation of the SiNW's.

In conclusion, abundant microtwins, stacking faults, and low-angle grain boundaries were analyzed in SiNW's using HREM. These planar defects may play an important role in the formation and the morphology of SiNW's.

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