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Growth morphology and micro-structural aspects of Si nanowires synthesized by laser ablation

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Abstract

Si nanowires (SiNWs) synthesized by laser ablation method exhibit different morphological characteristics such as straight, curved, kink, braided, and coiled shapes. These morphologies and their corresponding micro-structural aspects were examined in some details by transmission electron microscopy (TEM). It is found that the formation of various morphologies of SiNWs is closely related to the insertion of twins or the spatial twisting along the growth direction during the growth process of SiNWs. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

There has been an increasing interest in the investigation of one-dimensional nano-structures. Several experimental approaches to fabricate quantum wires, utilizing nano-fabrication techniques and crystal growth techniques, have been reported. Recently silicon nanowires (SiNWs) with nano-meter diameter have been successfully synthesized by laser ablation method [1,2]. The nano-meter-scale wires may lead to study of many new physical phenomena and promise in nano devices based on quasi-1D electron gas in the ultra-fine SiNWs. Preliminary measurements show that SiNWs have interesting physical properties that are different from conventional bulks materials and whiskers of Ge [3,4], Si [5,6], GaAs [7,8] grown by vapor–liquid–solid (VLS) mechanism. It is considered that these peculiar physical properties are mainly related to the quantum confinement effect related to reduced dimension of materials. The internal structure of these nanowires is closely related to the growth kinetics and will give rise to different morphological aspects of nanowires. In the present paper, the morphological aspects and corresponding

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microstructures of SiNWs have been studied by means of transmission electron microscopy. Our observations show that SiNWs exhibit a variety of morphological characteristics with straight, kink, curved, braided, and coiled shapes. The coiled shape attracted much attention especially. Growth of coiled crystal of fibers is very interesting in relation to its peculiar morphology, growth mechanism, as well as applications. To our knowledge, the microstructure and its impact on the morphology of these coiled-shaped nanowires remains an open question. Our results provide further understanding of the growth mechanism and physical properties of SiNWs.

2. Experiment

The system used to synthesize SiNWs is the same as that destined for the preparation of BN nanotubes [9]. Fig. 1 is the schematic of SiNWs growth apparatus. The target material was prepared by hot-pressing silicon powder (about 97 wt% of Si, and about 3 wt% of Fe as impurity), mixed with nano-sized Co–Ni catalyst (about 5 wt% each). The target was placed inside a quartz tube which was evacuated to about 20 mTorr, and then heated in a flow of argon at about 850°C for 4 h to allow degassing. After a further degassing at 1200°C for 20 h, the target was ablated by an excimer laser with wavelength of 248 nm at pressure of about 500 Torr. The ablated species self-organize into SiNWs. The dark yellow-colored, sponge-like product was found deposited on the quartz wall, just in front of the copper collector. A small piece of the fresh product was directly glued on a holey carbon film covering the copper grid destined for immediate TEM examination. Conventional TEM analysis in this work was carried out in a Philips-CM12 electron microscope. The HREM investigation was conducted using a JEM-2010 high-resolution electron microscope operating at 200 kV with point-to-point resolution of about 0.19 nm.

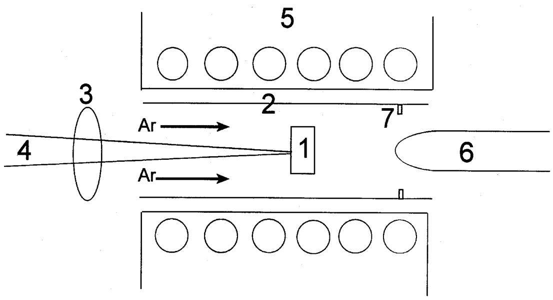

Fig. 1. Schematic of the SiNWs growth apparatus. The output from an excimer laser (4) is focused (3) onto a target (1) within a quartz tube (2). The reaction temperature is controlled by a furnace (5). The SiNWs are collected on the tube wall (7), just in front of the water-cooled collector (6).

3. Results and discussion

A survey of the morphology of the SiNWs is given in Fig. 2, which includes the straight, kink, curved, coiled, and braided morphologies. According to the TEM observation, it is found that the straight (marked with letter A), kinked (B) or smoothly curved (C) shapes are the main morphological characteristics of the SiNWs, and only a small fraction adopts the braided (in the upper-right inset of Fig. 2) and coiled (D) shapes. The diameter of straight, kink, or curved SiNWs (about 13 ± 3 nm) is smaller than that of the braided (about 60 nm) and coiled SiNWs (about 30 nm). Change in diameter along its length was seldom observed for a given SiNW. Systematic TEM observations show that the SiNWs with braided and coiled shapes can only exist when the diameter of nanowires is larger than 20 nm. The length of the SiNWs ranges from a few microns to hundreds microns. The selected-area electron diffraction (SAED) pattern taken from the SiNWs is shown in the upper-left inset of Fig. 2, and the diffraction rings reveal that the crystalline lattice parameter of the SiNWs is same as that of the bulk Si.

Coiled SiNWs synthesized by laser ablation exhibit various shapes as shown in Fig. 3. In most cases, the coil pitch is constant throughout a coil. Fig. 3a and Fig. 3b shows a regular coiled nanowire which has a constant coil diameter and coil pitch. But sometimes the coil pitch is not constant throughout a coil as shown in Fig. 3c and Fig. 3d. We also find that the coiled nanowire can be smoothly curved and forms a U-shape as shown

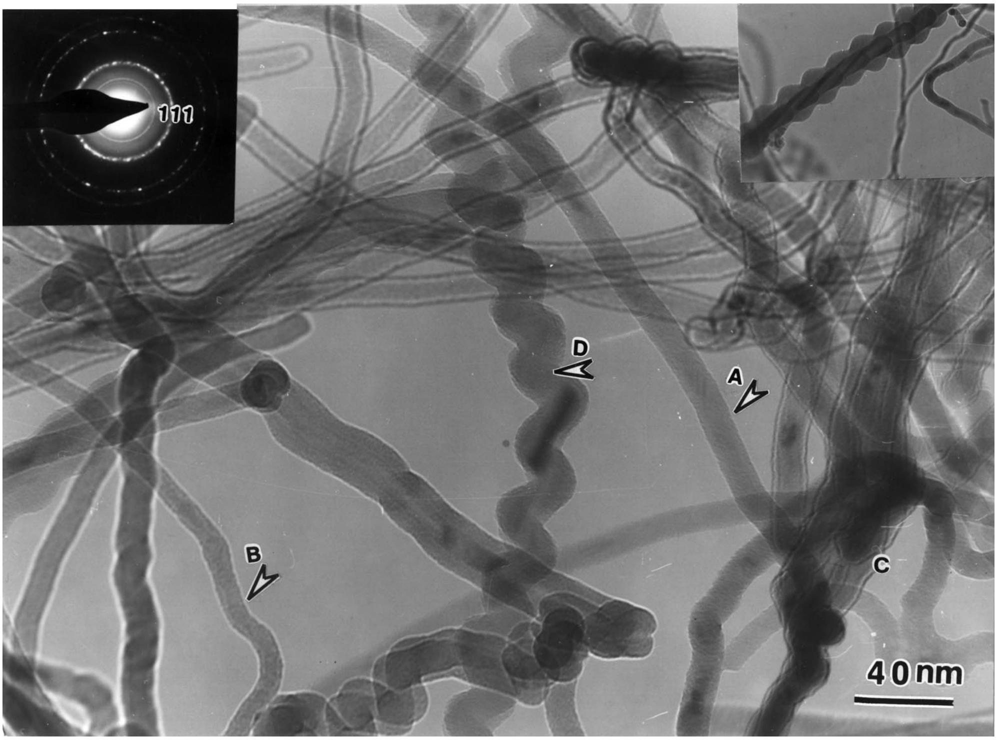

Fig. 2. A typical TEM image showing the general orphology of SiNWs including the straight, kink, curved, braided, and coiled forms.

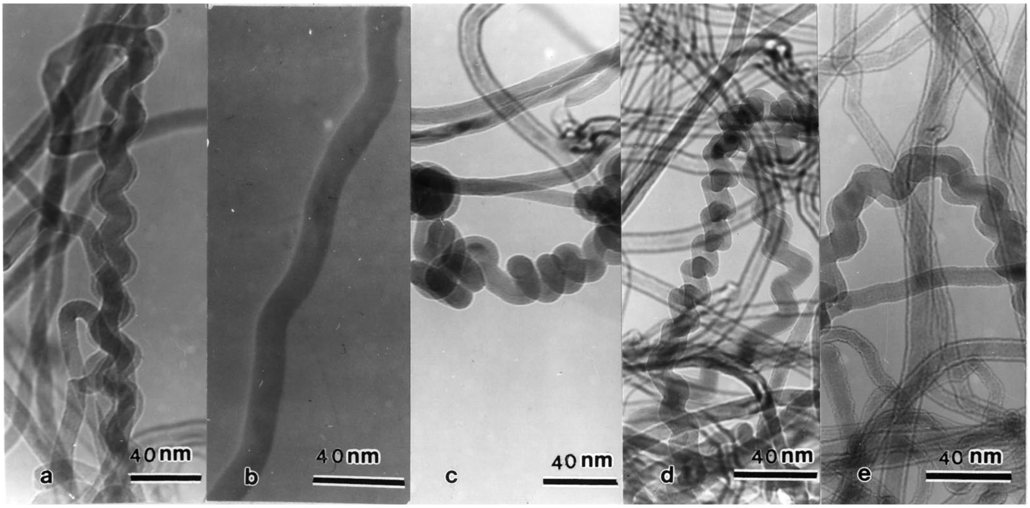

Fig. 3. Coiled SiNWs synthesized by laser ablation exhibit various shapes. (a) Helix-shaped SiNW having constant pitch along the axis of a coiled SiNWs. (b) A coiled SiNW with larger pitch angle than (a). (c) A complicated coiled SiNW. (d) Helix-shaped SiNW without constant pitch angle (e) A U-turn coiled SiNW.

in Fig. 3e. For the coiled SiNWs, the radius of cylinder on which the helix is estimated ranging from 3 nm to a few tens nano-meter. The period of the helix ranges from 6 nm to a few hundreds nano-meter.

In order to reveal the relationship between the morphology and microstructure, the high-resolution transmission electron microscopy image (HRTEM) was employed to investigate the SiNWs at atomic scale. The HREM images in Fig. 4 show the representative micro-structural characteristics of two individual straight SiNWs. A thin amorphous layer (about 2 nm in thickness) is visible around the SiNWs, which turns out to be amorphous silicon oxide resulting from surface oxidation. The image in Fig. 4a shows a single SiNW which has smooth surface. It is found that the growth direction of the nanowire is along the [−2 1 1] axis, in other words, the (1 1 1) planes is parallel to the growth axis of the SiNWs. Fig. 4b shows the image of another SiNWs which has rough surface. According to this HREM image, it can be found that the surface roughness is caused by the growth of zigzag-shaped lamellar twins.

Fig. 5 reveals the micro-structural detail of the kink and curved SiNWs. From the HREM image of Fig. 5a, we can find that the kink site actually corresponds to the insertion of a twin. Fig. 5b shows the existence of a micro-twin in a highly curved SiNW.

It was found that SiNWs also adopt braided shapes as shown in the inset of Fig. 2. These nanowires consist of a row of knots and necks with approximately an equal distance between them. Its diameter shows a periodic variation along the growth direction. The periodicity is not strict and differs from various nanowires. We speculate that formation of braided shape is an intrinsic nature related to the growth process of SiNWs. Fig. 6 is a HREM image of a segment of braided SiNW. The incident electron beam is parallel to the [1 1 0] axis. From this HREM image, we can find that the knots are connected by the necks to form dumbbell shape. At the neck site, there exist many micro-twins as indexed with the arrows. The growth direction is along [1 1 1] direction. Owing to the fact that the twins oriented slight differently with respect to the incident electron beam, which results in a different

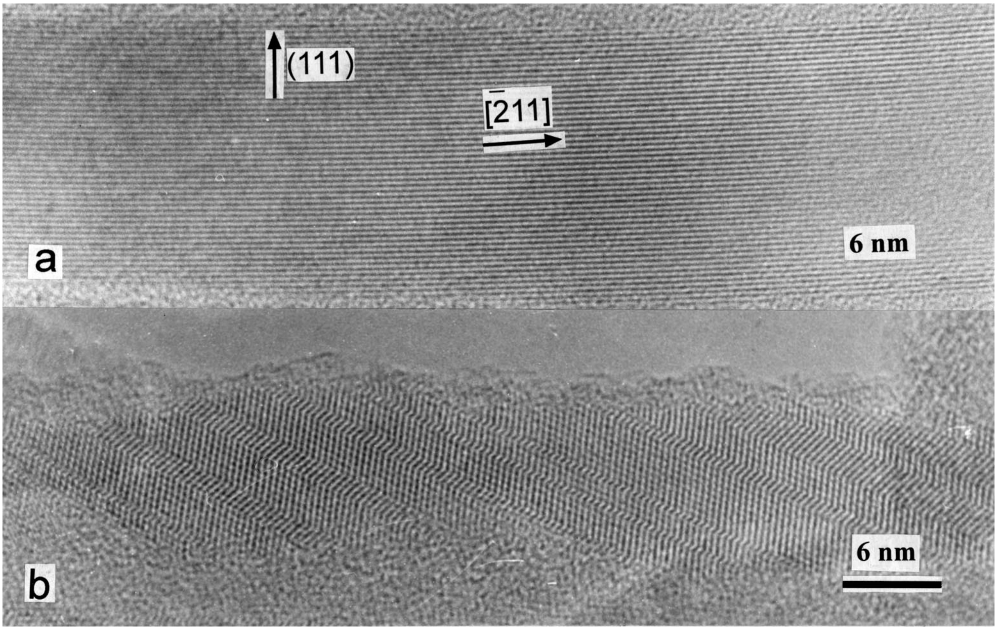

Fig. 4. HREM images of microstructure of two straight SiNWs. (a) A SiNW with a set of (1 1 1) plane parallel to the growth direction has smooth out surface. (b) A SiNW with zigzag-shaped lamellar twins growth has rough surface.

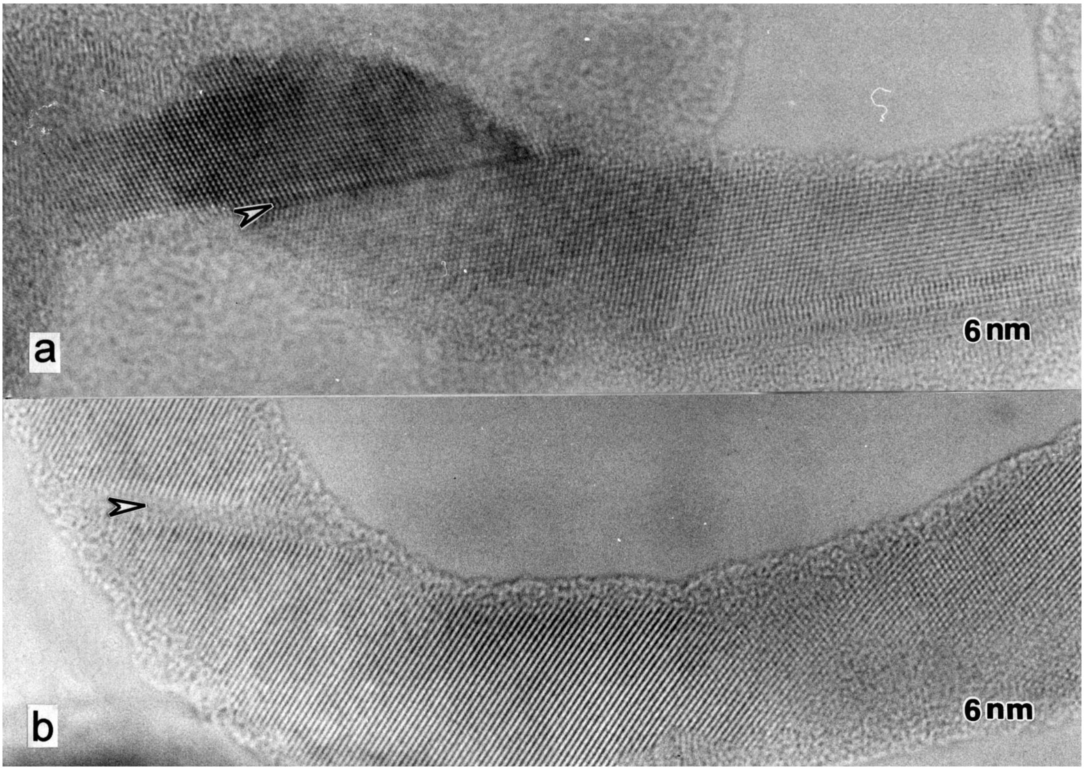

Fig. 5. Micro-structural aspects of SiNWs with kink or curved shape. (a) Kink site actually corresponding to a twin boundary. (b) Highly curved part actually corresponding to the insertion of micro-twins.

electron diffraction contrast in a low magnification image, so the bright and dark contrast in the braided SiNWs results from the difference in electron diffraction conditions on two sides of the twin boundary as shown in an up-right inset in Fig. 2.

The HREM image in Fig. 7 shows the representative micro-structural features of an individual coiled SiNW with a diameter around 30 nm and SiO_2 amorphous surface coating layer. The areas labeled with letter A, C are along the [0 1 1] zone axis. In area B, only one-dimensional lattice fringes are visible. The spacing between visible fringes is 0.19 nm, which corresponds to (0 2 2) plane of a silicon structure. It is visible that the (0 2 2) lattice fringes is continuous in area A, B, and C. The twisting, by keeping the same (0 2 2) plane unchanged, is often observed in the coiled SiNWs in our experiment. Twins are also formed indicated with letter of TB at the kink site of the coiled SiNWs. From this image, we can find that the growth direction of SiNWs shifts from [−2, −1, 1] to [2, −1, 1] in area A. In area B, the twisting is occurred by keeping the continuation of (0 2 2) plane with the area A and area C. In area C, the growth direction is then changed to [2, −1, 1]. The coiling of the SiNWs can be modeled as consisting of segments with different orientation but with a similar structure as the straight SiNWs. According to our observation, there are mainly two ways to connect the straight segment of nanowires with a coil shape. The first is the insertions of twins or stacking faults along the growth direction of the SiNWs. This type of coiling is observed when the [0 1 1] zone axis of SiNWs is parallel to the incident beam and the orientation change was introduced by formation of (1 1 1) twin or (1 1 1) stacking faults. The second type of coiling is the spatial twisting, by which the zone axis of [0 1 1] is

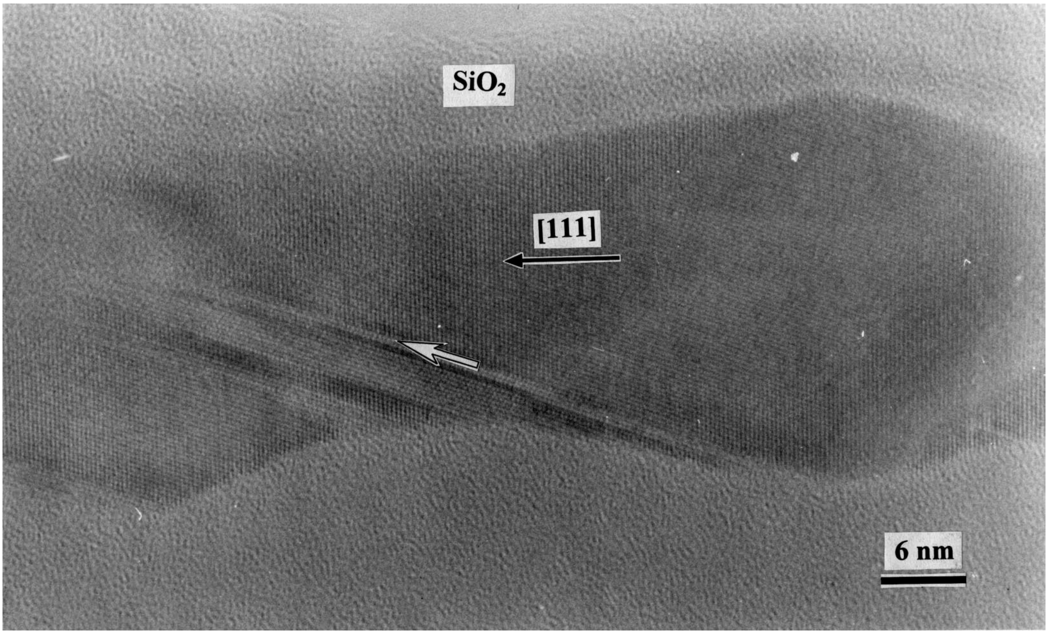

Fig. 6. HREM image of a braided SiNW with about diameter of 70 nm. The incident electron beam is along the [1 1 0] axis. The growth direction of nanowire is along [1 1 1]. It can be found that there exists twins at the necks.

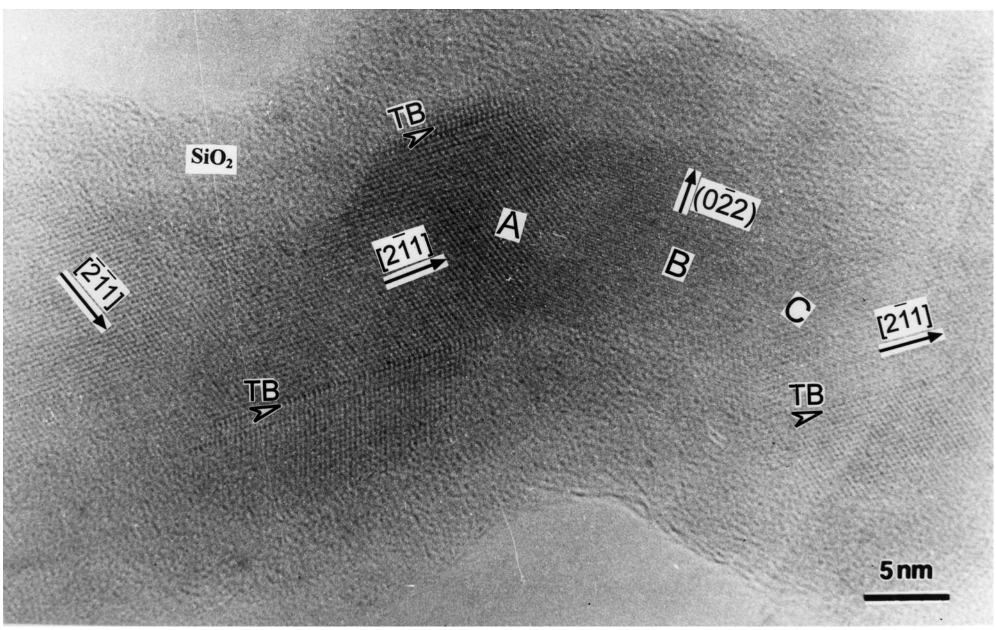

Fig. 7. Micro-structural aspects of a coiled SiNW. The growth direction of nanowire shifts from [− 2, − 1, 1] to [2, − 1, 1] in area A. Spatial twisting is occurred in area B by keeping the continuation of (0 2 2) plane with area A and C. The growth direction is switched to [2, − 1, 1] in area C.

changed as shown in the area B, but keeping the continuation of (0 2 2) planes along the growth direction of the SiNWs. According to the HREM investigation, it is likely that a regular coiled SiNW results from a periodic continuation of this kind of structural aspect along the growth direction of the SiNWs. And the coiled pitch may be related to the twin boundary structure. It has been well known that coiled-shaped carbon nano-tubules were obtained by thermal decomposition of hydrocarbons catalyzed by a metal [10], And the coiling of carbon nano-tubule is explained by a periodic distribution of pentagon–heptagon pair dislocations [11], while in the SiNWs, it is interesting to note that the coiling is dependent on the periodic change of growth direction along the length of the SiNWs.

It is known that whisker may deform with kink or coiling under a compressive stress along a direction parallel to the length of the whisker. The morphological aspects that are observed in our experiment have not been deformed intentionally. The HREM images of coiled SiNWs also indicate that there are not plastic deformation at the junctions between two straight segments of a coiled SiNWs. On the other hand, it should be noted that although the coiled pitch and coiled diameter are periodic for a SiNW, they are different for various SiNWs. So it is likely that the cause of coiling of SiNWs is also intrinsic to the growth process, otherwise the coiled pitch and diameter would vary synchronously.

Upon above experimental results, we can see that (1 1 1) twins or stacking faults play an important role in the determination of the morphologies of the SiNWs. Because the (1 1 1) plane family is the densest packed plane with the lowest energy in silicon structure, twins or stacking faults are easily introduced by change of the plane stacking sequence. The twins or stacking faults can meditate the further growth of crystal, and result in the preferred growth direction. Owing to the fact that the growth of SiNWs by laser ablation is a non-equilibrium course, it is likely that Si atoms position themselves in re-entrant sites will be more stable. The insertion of twin will give rise to re-entrant corners, thus these re-entrant corners provide preferred sites for the nucleation of new layers. A new plane forms at the re-entrant site can grow rapidly because there are stable positions at step site of the propagating plane. So the growth direction of the SiNWs can be changed by the insertion of twins or stacking faults. As a result, different morphological characteristics are developed.

4. Conclusions

In conclusion, the morphologies and microstructural features of coiled SiNWs synthesized by laser ablation were examined by transmission electron microscopy. It is found that the formation of different morphological aspects is closely related to the insertion of twin or stacking faults and the change of the growth direction of SiNWs along the length.

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