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SYNTHESIS OF NANO-SCALE SILICON WIRES BY EXCIMER LASER ABLATION AT HIGH TEMPERATURE

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We report below synthesis of nano-scale silicon wires by using laser ablation at high temperature. By this approach we have been able to produce silicon nano wires (SiNW's) with a very high yield, a uniform diameter distribution and a high purity. The structure, morphology and chemical composition of the SiNWs have been characterized by using high resolution X-ray diffraction (XRD), high resolution electron microscopy (HREM), as well as spectroscopy of energy dispersive X-ray fluorescence (EDAX). Our results should be of great interest to researchers working on mesoscopic physical phenomena, such as quantum confinement effects related to materials of reduced dimensions and should lead to the development of new applications for nano-scale devices, together with providing a powerful method for synthesis of similar one-dimensional conducting and semi-conducting wire. © 1998 Elsevier Science Ltd

1. INTRODUCTION

With development of the contemporary science, one needs to synthesize and to well understand new materials of reduced dimensions such as two-dimensional quantum wells, one-dimensional wires and quantum dots. As a result, the discovery of carbon nanotubes [1], carbide nanorods, gallium nitride nanorods [2–4] and porous silicon and silicon nano-crystallite has attracted much attention for scientists from a diverse range of research fields and has stimulated intensive research interest on their physical properties and on quantum confinement effects [5–8]. To our knowledge, no synthesis of SiNWs has been reported to date [9], although micro-sized silicon whiskers have often been mentioned [10, 11]. We will report below the successful synthesis of SiNWs by using laser ablation at high temperature.

2. EXPERIMENTAL

The system we used to synthesize SiNWs is the same as that destined to preparation of BN nanotubes [12]. The target material was prepared by mixing silicon powder (about 97 wt.% of silicon in purity and about 3 wt.% of Fe as impurity) with nano-sized Ni and Co powder (about 5 wt.% each). The mixed powder was hot-pressed at 150°C to form a plate target. The target was placed into a ϕ 42 mm × 750 mm long quartz tube. The quartz tube was firstly pumped to about 20 mTorr. The target was 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 using an excimer laser with a wavelength of 248 nm at pressure of about 500 Torr. The laser beam was focused on the target to a spot of 1 mm × 3 mm by using 500 mm focal lens and the target was ablated at 1200°C. The frequency of the laser beam is 10 Hz. The average energy per pulse is about 400 mJ.

The morphology and composition analysis of the SiNWs were performed by means of a Philips-CM 20 transmission electron microscope equipped with an EDAX detector. XRD characterization was realized using a Philips X'Pert-MPD Diffractor. High resolution electron microscopy (HREM) was conducted by using a Jeol-2010 microscope with a point-to-point resolution of about 0.19 nm.

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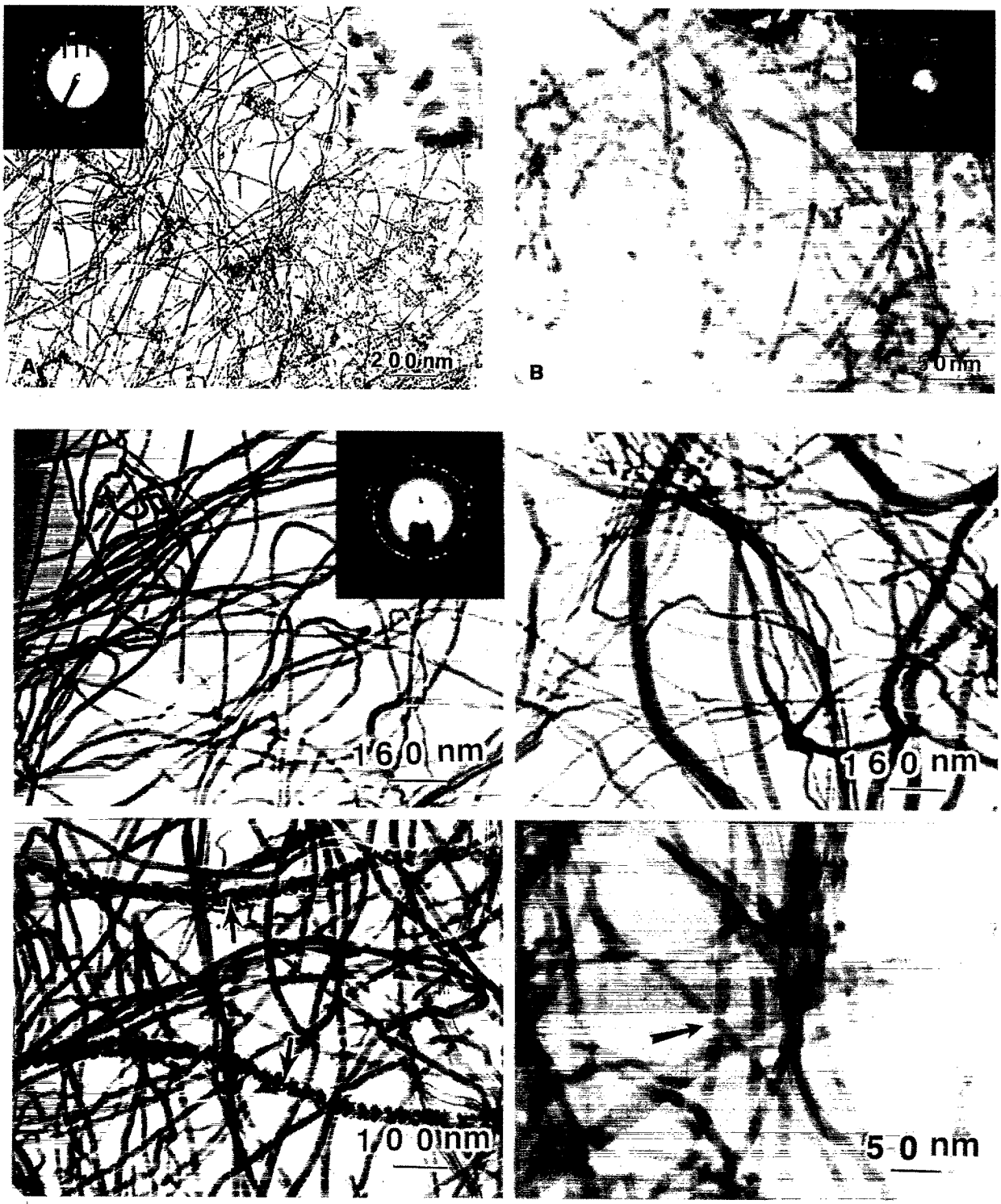
A
200 nm
B
160 nm
160 nm
100 nm
50 nm
C

3. RESULTS AND DISCUSSION

In case of hot-pressed targets, the ablated species self-organize into SiNWs and a dark yellow colored, sponge-like product was found deposited as a round ring with a width of about 10 mm on the quartz tube wall, just in front of the copper collector. It should be noted that production of SiNWs is perfectly reproducible in our approach. The fresh-made products were sealed in an argon atmosphere to prevent any surface oxidation. A small piece was torn out from the fresh-made sponge-like product and it was placed onto a copper grid destined to immediate transmission electron microscopy analysis.

The micrographs reported in Fig. 1 are representative of the general morphology of SiNWs which were grown under different conditions. Figure 1(a) shows a low magnification image of SiNWs produced from a target containing a Co–Ni catalysis. Most of the visible SiNWs have a curved-shape morphology and some of them even appear largely coiled (insert on upper-right). More than 99% of the product is estimated to be SiNWs. The corresponding selected area electron diffraction (SAED) pattern is shown in insert on the left part of Fig. 1. It is a spotty ring pattern that is typical of polycrystalline silicon. In that pattern, the first, second and third order rings respectively correspond to the {1 1 1}, {2 2 0} and {3 1 1} lattice plane families, with an interplane spacing of about 0.31 nm, 0.19 nm and 0.16 nm, which is consistent with values usually obtained for bulk silicon.

The magnified micrograph shown in Fig. 1(b) reveals the diameter uniformity of the SiNWs resulting from catalyst-containing targets, as well as their smooth curved morphology. We found that most of the SiNWs have a diameter of 13 ± 3 nm, while their length ranges from a few tens μm to hundreds μm (it is usually quite difficult to find their ends). Insert shows a SAED pattern along [110] zone axis taken from a single SiNW.

The morphology of the SiNWs produced from Co–Ni catalysts-free targets is shown in Fig. 1(c). It can be seen that while some parts of the SiNWs exhibit an uniform diameter (upper-left image), most of the SiNWs have a diameter that appear not uniform at all, ranging from 15 nm to 60 nm (upper-right image), when it is compared to that of the SiNWs resulting from catalyst-containing targets. It is noted that this interesting phenomenon is similar to what is observed for single walled carbon nanotubes that are prepared using a similar method [13, 14]. The corresponding SAED pattern is shown in insert. Very peculiar braid-like morphology (lower-left image) and branched contrast (lower-right image) are visible.

The chemical composition of the SiNWs was determined using EDAX. In the EDAX spectrum of SiNWs produced in a careful run [Fig. 2(a)], only one peak is visible, which corresponds to silicon, indicating that the obtained sponge-like product is made of pure silicon. No evidence of existence of Ni or Co is detected in EDAX analysis. Though Co and Ni catalysts mixed in target may influence the diameter of SiNW as is revealed in Fig. 1(c), their role in formation of SiNW seems not determinant in formation of SiNW. Instead, we believe that Fe atoms which appear as impurity in the target of silicon powder act as catalyst and are closely involved in formation of SiNW and hence play an important role in SiNW growth.

The structure of the sponge-like SiNWs product was characterized by means of high resolution XRD. The XRD spectrum of the SiNWs that is shown in Fig. 3 contains nine peaks which are clearly distinguishable. All of them can be perfectly indexed to crystalline silicon, not only in peak position, but also in their relative intensity. The spectrum contains no impurity phases. XRD spectra of SiNWs produced from targets with or without catalysts are similar. The lattice parameter of the SiNWs, as calculated from the value of the most intense (1 1 1) peak ($d = 0.3147$ nm) is equal to $a_{\mathrm{SiNW}} = 0.5450$ nm, that is 0.368% larger than the standard value $a_{\mathrm{Si}} = 0.5430$ nm for bulk silicon, what is indicative of a slight lattice expansion and distortion of the SiNW structure. In order to help the readers to make a comparison, a XRD spectrum of silicon powder is also shown together with that of the SiNWs.

HREM analysis provided additional structure details of the SiNWs. Figure 4(a) shows an HREM image of a single SiNW with a diameter of about 11 nm. The incident electron beam is parallel to the [1 1 0] zone axis. The interplanar spacing is about 0.31 nm,

Fig. 1. (a) Representative micrograph of the general morphology of a sponge-like product resulting from catalyst-containing targets. It reveals that the product consist of pure SiNWs. The insert on the left shows the corresponding SAED pattern that appears composed of spotty rings, while the insert on the right shows highly curved SiNWs. (b) Representative micrograph showing the uniformity of the SiNW diameter which ranges from about 10 nm to 16 nm. Most of the SiNWs have a diameter of about 13 nm. Insert shows an apparent [110] SAED pattern taken on a single SiNW. (c) Morphology of SiNW from target without Co–Ni catalysts. A small portion of the SiNW have an uniform diameter (upper-left) and most of the diameter is not uniform ranging from 15 nm to 60 nm (upper-right). Braid-like (lower-left) and branched morphology (lower-right) are visible.

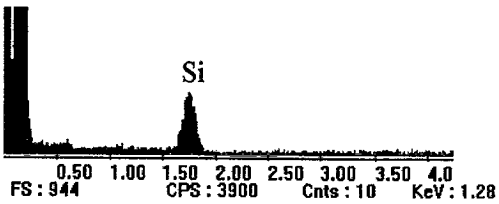

Fig. 2. EDAX spectra reveal that the SiNWs are composed of pure silicon.

corresponding to the {1 1 1} plane of silicon. The two-dimensional lattice image also reveals that the SiNW is single crystalline. The HREM image shown in Fig. 4(b) shows that the (1 1 1) lattice fringes are parallel to a segment of a SiNW with a diameter of about 15 nm. The {1 1 1} planes family is the most dense plane with the lowest energy, so it may play an important role in SiNW growth. In many case in HREM observation it was found the axis direction of the segment is parallel to the [2 1 1] direction and it seems that this direction is a general direction of the SiNW growth. A thin amorphous layer is visible close by the SiNW, presumably due to surface oxidation during analysis. Figure 4(c) shows the continuous {1 1 1} lattice fringes of part of a smooth-curved SiNW, revealing the growth mechanism of the SiNW, that is, though the growth direction change smoothly as the SiNW bend, the crystalline direction remain the same. Micro-twins are frequently visible (arrow-heads marked and shown in insert) in the SiNW which must play an important role in the SiNW growth.

Preliminary measurement of SiNW photo-luminescence shows that it is different from that of bulk silicon, although it was recently reported that micro-sized silicon filaments exhibit a visible light photoluminescence [10]. A detailed study of growth mechanism, microstructure and physical properties of the present SiNW is under way and will be published in separate papers.

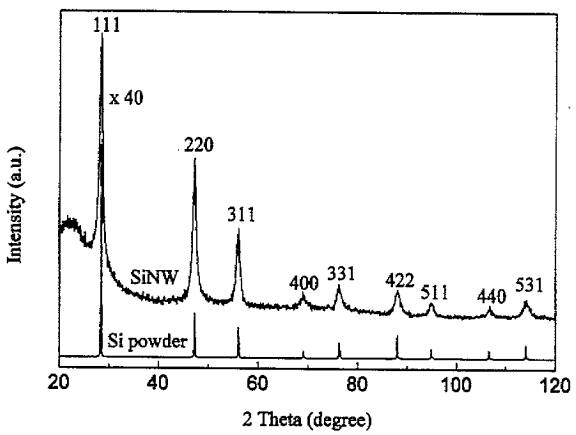

Fig. 3. XRD spectrum of SiNWs. All the peaks can be perfectly indexed to crystalline silicon both in peak position and in their relative intensity. A XRD spectrum of silicon powder is also shown for comparison.

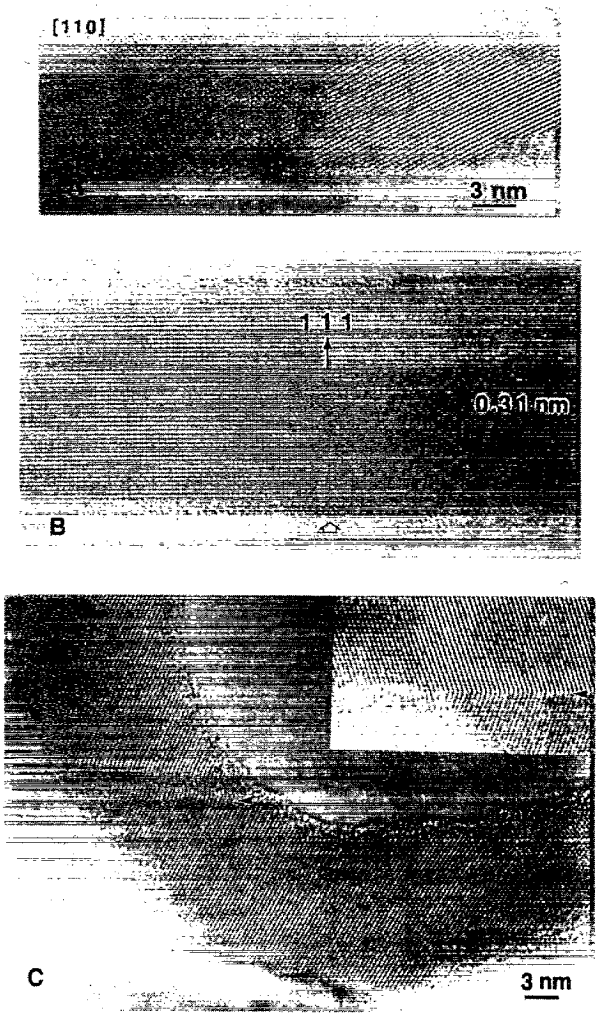

Fig. 4. (a) HREM image ([1 1 0] zone axis) of a single SiNW with a diameter of about 11 nm. (b) HREM image showing (1 1 1) lattice fringes that are parallel to a segment of a single SiNW and the general growth direction is [2 1 1] direction. A thin amorphous layer is visible near by the SiNW, that is presumably due to surface oxidation. (c) HREM image of a smoothly curved SiNW. {1 1 1} lattice fringes remain unchanged though the SiNW curves smoothly. Microtwins may play important role in SiNW growth.

4. CONCLUSIONS

We have been able to synthesize SiNWs of high purity, high yield and uniform diameter distribution by using laser ablation method. The impact of our results on fundamental research is obvious. SiNWs can provide theorists with an exciting opportunity to study some mesoscopic physical phenomena related to materials of reduced dimensions, such as quantum confinement

effects. In practice, the silicon-based electronics technology is one of the greatest successes of this century and as a result, the well-established silicon-based modern electronics technologies make it possible to use the present SiNWs for future nano-scale device applications and through further doping of the SiNWs a large variety of new semiconducting nanowires should be soon available. The method we present here should also become a powerful tool to synthesize new one-dimensional, semiconducting or conducting wires.

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