

# Straightening Suspended Single Walled Carbon Nanotubes by Ion Irradiation

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## ABSTRACT

Single walled carbon nanotubes grown suspended between pillars of Si/SiO<sub>2</sub> structures are straightened by ion beam scans. In addition, the ion irradiation selectively removes nanotubes lying on the substrate, leaving the suspended nanotubes in place. This strategy provides a facile way to produce large area connected networks of suspended straight nanotubes. Although ion irradiation induces structural modifications to nanotubes and introduces defects into the nanotube lattice, the form and dimensions of the nanotubes remain close to that of original grown structures. Nanotube networks consisting of perfectly straight and suspended structures could serve as a platform for various applications.

Recent progress in the controlled growth of carbon nanotubes allows the growth of large area networks of interconnected single walled nanotubes.<sup>1–4</sup> This is accomplished by chemical vapor deposition (CVD) of methane gas over catalyst coated lithographically patterned substrates. After CVD growth, the substrate patterns are decorated by individual or small bundles of single walled nanotubes, overhanging from the pillars and lying on the substrate. Although large area networks of such nanotubes have been grown, there are still several issues that need to be addressed to particularly tailor well-ordered nanotube networks. One issue relates to the overall form of the nanotube cables that bridge the substrate features. Normally growth produces nanotubes that are not straight between pillars and that sag because the lengths of nanotubes grown are not equivalent to the separation between pillars. This produces a high percentage of the nanotube lengths in networks having improper orientation with respect to the overall alignment of the nanotubes in the network and could be a detriment in applications such as electrical wires/interconnects.<sup>5–6</sup> This could lead to shorting between wires, particularly if there are also nanotubes on the substrate that do not conform to the suspended network of nanotubes above. Similar is the case if the nanotube network needs to be used as a versatile template for attaching molecules and using them for applications such as sensors.<sup>7</sup> The ideal scenario in such cases should consist of nanotubes

that are perfectly straight between the various growth points on the substrate and consisting of only suspended nanotubes above the substrate. Such well-ordered networks are difficult to fabricate.

The present experimental results reported here focus on the modification of suspended single walled carbon nanotube (SWNT) networks using Ga<sup>+</sup> ion irradiation in a focused ion beam (FIB) instrument. For the substrate preparation, Si (100) and SiO<sub>2</sub> (300 nm)/Si (100) were patterned into the cylindrical pillar shape (200 nm diameter and 300 nm height with 250 nm distance between pillars) using synchrotron-radiation lithography.<sup>8</sup> Thin Fe film was deposited on this patterned substrate as catalyst materials, and SWNTs were grown using our conventional methane CVD method.<sup>9</sup> Then, the resulting SWNT networks were irradiated with Ga<sup>+</sup> ions using a FIB with an accelerating voltage of 30 keV (Hitachi FB-2000A). High-resolution scanning electron microscopy (Hitachi S-5000 HRSEM) was employed to observe the morphology difference between as-grown and Ga<sup>+</sup>-ion irradiated suspended carbon nanotube networks on the designed substrates, and the typical ion dose was around  $1.5 \times 10^{14}$  ions/cm<sup>2</sup>. Raman spectroscopy using 785 nm wavelength was employed to characterize the structural changes of suspended carbon nanotubes after Ga<sup>+</sup>-ion irradiation.

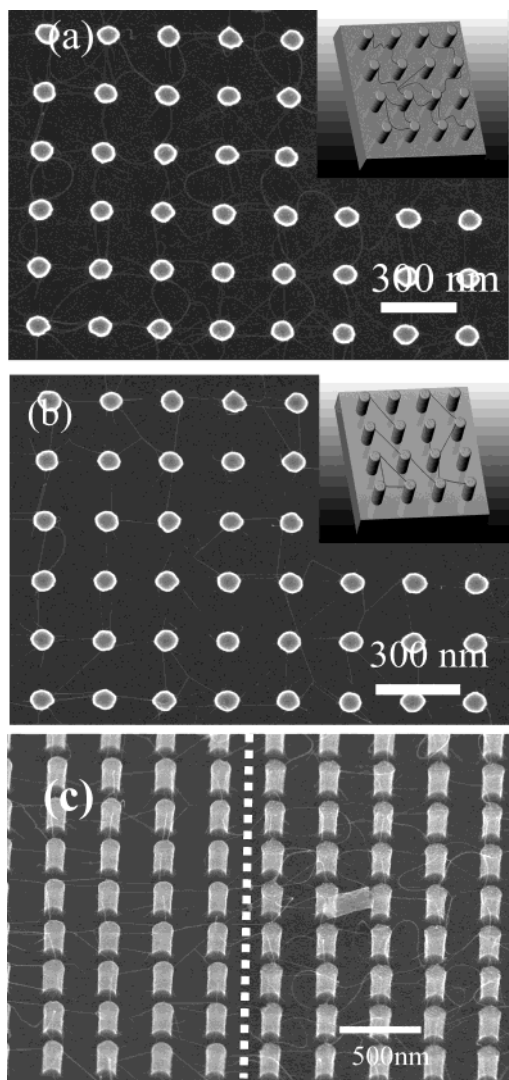
The representative example of the as-grown and modified SWNT networks on the nanoscale patterned silicon pillar structures is shown in Figure 1a,b. Figure 1a is the top view of as-grown SWNTs forming self-directed networks on patterned pillar structures. Most of the suspended nanotubes are curved and do not connect the pillars along straight paths.

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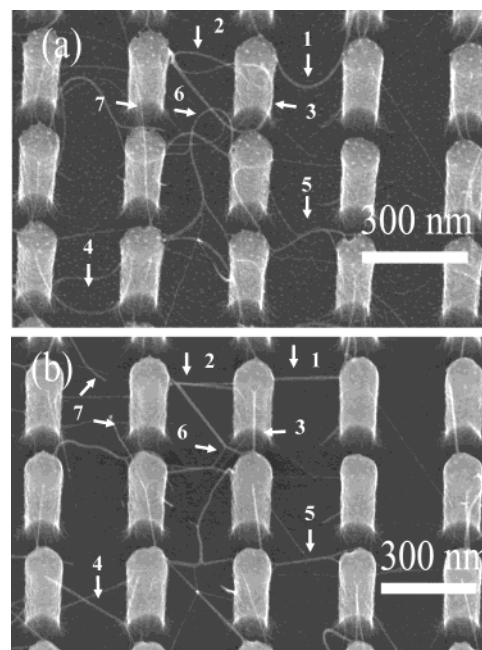
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**Figure 1.** SEM images with inserted schematics show SWNT networks formed on submicron size patterned Si pillars (200 nm diameter, 300 nm height, and 250 nm distance between pillars) (a) before the  $\text{Ga}^+$  ion irradiation and (b) after the  $\text{Ga}^+$  ion irradiation in the same position of the sample. Note that most of the curved, as-grown SWNTs were straightened after  $\text{Ga}^+$  ion irradiation. (c) A tilted HRSEM image shows both the as-grown suspended SWNTs region (right side of the image) and straightened SWNTs in the  $\text{Ga}^+$  ion irradiated region (left side of the image) in the substrate. The white square-dot line is the boundary between areas exposed and unexposed by the FIB.

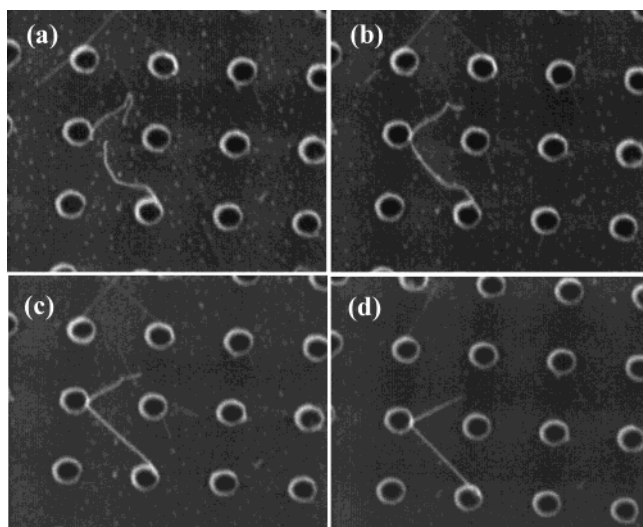
However, after a few seconds of irradiation of this SWNT network by the ion beam, striking changes in the overall structure of distributed SWNTs in the network are observed. Figure 1b shows that most of the originally curved as-grown suspended SWNTs connecting pillars have been permanently straightened after the ion beam scans. This straightening effect occurred regardless of the growth direction and overall shape of suspended SWNTs. Therefore, the predetermined original orientation and distribution scheme of as-grown SWNTs in the network are basically not altered. Figure 1c is the tilted SEM image of another large area SWNT network, partially irradiated with  $\text{Ga}^+$  ions. From the SEM image, it is clearly seen that in the  $\text{Ga}^+$ -ion irradiated area (the left side of Figure 1c separated from the un-irradiated area by



**Figure 2.** Higher magnification tilted SEM images showing suspended SWNT networks (a) before and (b) after  $\text{Ga}^+$  ion irradiation. Numbered white arrows are indicating the morphology changes in various types of suspended SWNT bundles before and after  $\text{Ga}^+$  ion irradiation at the same position of substrate: (1, 2, and 3) SWNT bridges between nearest pillars, (4) SWNT bridge between second nearest pillars, (5,6) Y or double Y SWNT junctions, and (7) very long suspended SWNTs.

the dotted line boundary), nearly all the suspended SWNTs became straightened. On the right portion of Figure 1c, where ion irradiation was not done, all of the SWNTs remain as original with significant deviation from the ideal straight oriented network. The results show that controlled area  $\text{Ga}^+$  ion exposure can be used to selectively and locally modify SWNT networks grown on patterned substrate structures.

Detailed information on the effects of  $\text{Ga}^+$  ion treatment on the modifications of SWNT networks could be obtained through higher magnification SEM observation (Figure 2) and series of FIB images (Figure 3) of locally irradiated areas. As shown in Figure 2a, there are various types of curved and suspended SWNTs in the arrays before ion irradiation. Most of the SWNTs (or small bundles of these consisting of 1–5 nanotubes) connect nearest-neighbor pillars (see arrows 1, 2, and 3), but occasionally connections between second-nearest neighbors (see arrow 4) and much longer SWNT crossing over the substrate area (arrow 5) and even junctions (Y or double Y shapes) between nanotubes (arrows 6 and 7) are all seen in the as-grown SWNT networks. After irradiating these various types of SWNTs in the network (Figure 2b), it is clearly observed that straightening occurred not only in the nearest and second nearest SWNT bridges between the patterned pillars but also in the curved SWNTs that form Y junctions. The middle sections of the long SWNTs have been destroyed and removed during irradiation, resulting in two separate isolated suspended tubes. This points to another feature of the effect of ion irradiation on the grown nanotube networks. It is seen that nanotubes and parts of nanotubes that are in contact with



**Figure 3.** Series of FIB images showing the sequential straightening of suspended SWNTs on the patterned pillars and selective removal of SWNTs on the substrate (a) before Ga ion exposure, (b) after 4 Ga<sup>+</sup> ion beam scans ( $7.48 \times 10^{13}$  ions/cm<sup>2</sup>), (c) after 12 Ga<sup>+</sup> ion beam scans ( $2.24 \times 10^{14}$  ions/cm<sup>2</sup>), (d) after 16 Ga<sup>+</sup> ion beam scans ( $2.99 \times 10^{14}$  ions/cm<sup>2</sup>).

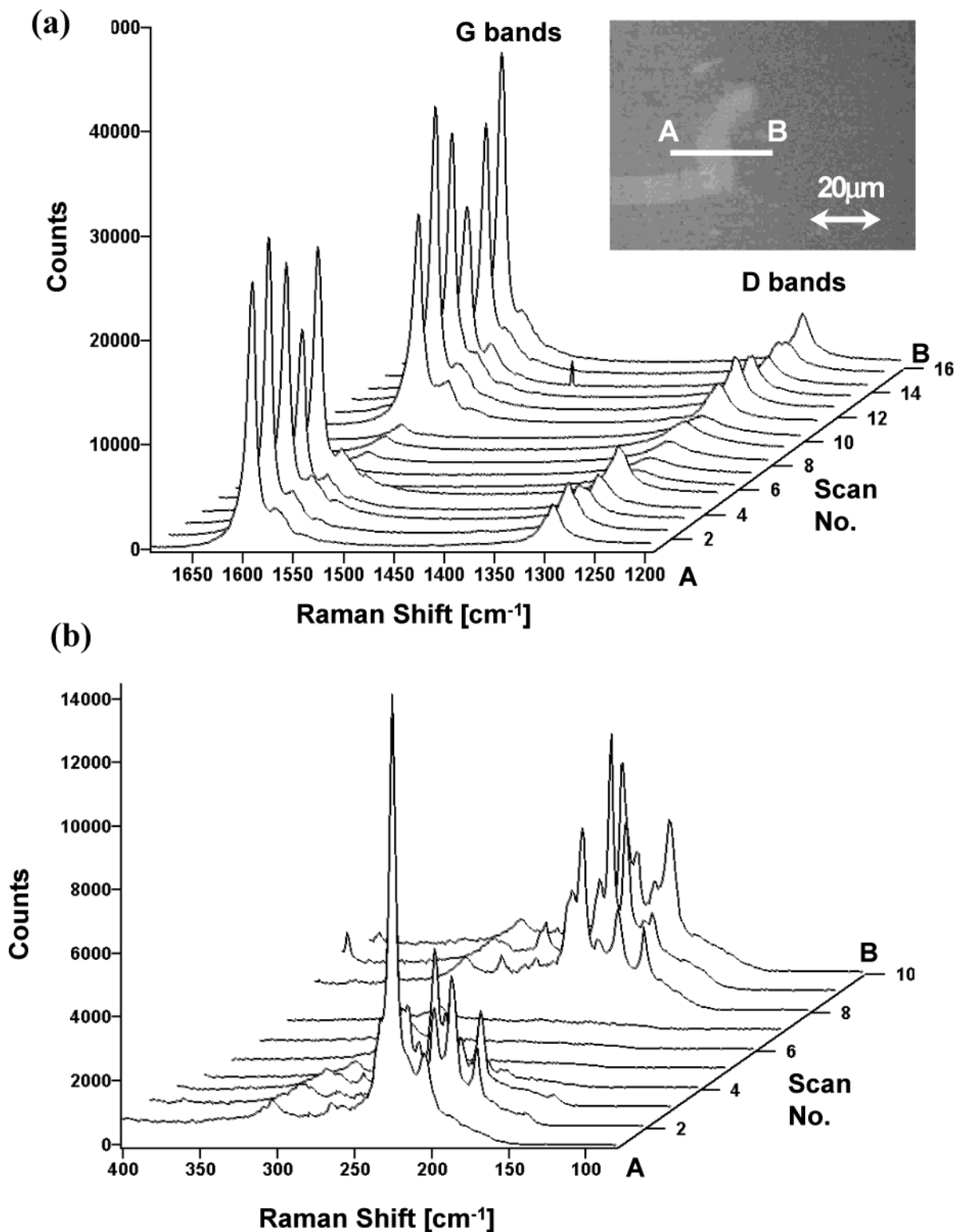
substrate are damaged much faster than those suspended between pillars; this provides a way to remove the nanotube that are on the substrate and leave only suspended nanotubes intact in the networks.

Figure 3 is a series of FIB images showing the sequential straightening of suspended SWNTs and the selective removal of the nanotubes lying on the substrate. Two isolated curled up SWNTs near two adjacent pillars are shown in focus with others in Figure 3a. After 4 Ga<sup>+</sup> ion beam scans, the initial straightening process occurs and one of the SWNTs starts to straighten and gets connected the second nearest pillar (Figure 3b). Increasing the number of Ga<sup>+</sup> ion scans results in further straightening of these two SWNTs (Figure 3c). Finally, after 16 Ga<sup>+</sup> ion beam scans, perfectly straight SWNTs suspended between pillars are obtained (Figure 3d). In addition to the straightening effect, the selective removal process of SWNTs and bundles is also seen simultaneously during ion irradiation in the sequential FIB images (Figure 3). It is also noteworthy that many of the Fe nanoparticles (size approximately 6–10 nm) formed during CVD on the substrates have also been removed during ion irradiation. Recently, Zhong et al. have shown in their simulation studies that ion induced surface smoothing could occur by a combination of burrowing and wetting processes during irradiation.<sup>10</sup> The different rates of damage induced in the nanotubes that are suspended versus those on the substrates may be related to the damage cross-sections and penetration depths of ions in an isolated thin structure versus those that are on the substrate material. In the former the ions could be nearly transparent and could cause relatively small amount of damage in the structure. When the nanotubes lie on the Si substrate and have an interface, irradiation could promote some mixing between atoms (carbon and Si), leading to a faster damage rate and destruction of the nanotubes.

The structure of suspended SWNT networks after a high

dose of Ga<sup>+</sup> ion irradiation has been analyzed by Raman spectroscopy. Figure 4 shows an optical microscope image and Raman spectra observed from suspended SWNT networks on pillar structures. The relatively bright band appearing in the optical microscope image in Figure 4a corresponds to the selectively Ga<sup>+</sup> ion irradiated region on the large area suspended SWNT networks. Figure 4a shows typical Raman spectra in the spectral range of 1200–1700 cm<sup>-1</sup>, in which we commonly observe the G band, ascribed to tangential modes of the graphene structure, and the disorder-induced D band, activated by the presence of defects or by the finite size of the nanotube. From ion unexposed sample areas, distinct G bands and D bands are observed at around 1590 cm<sup>-1</sup> and 1290 cm<sup>-1</sup>, similar to our previous result of suspended SWNTs.<sup>3</sup> However, in the ion irradiated region, the Ga<sup>+</sup> ion irradiation caused the G band to decrease in intensity to 1/20 and satellite fine structures observed at the lower frequency side of the principal G band to disappear completely. These fine structures are caused by zone folding of phonon dispersion along the circumferential direction of the CNT. Therefore, their disappearance means that the crystal ordering of CNTs along the circumference direction becomes considerably lower by the ion irradiation. On the other hand, the D-band intensities are reduced only by 30% despite the Ga ion irradiation. Consequently, the G/D ratio, which is related to the cluster size of graphene sheets, decreases from 4.5 to 0.3 by the irradiation. These results indicate that the Ga ions could have introduced defects into the graphene structure of the SWNTs, although the basic graphene structure partially survives the Ga ion irradiation. The amount of damage will depend on the actual dose of the ion irradiation. The introduction of defects into the SWNT structures is also observed in the low-frequency Raman spectra at the RBM region as shown in Figure 4b. SWNTs give rise to several RBM signals in each spectrum from the unexposed area and it corresponds to the SWNT diameter of 0.8–1.3 nm. However, the Ga<sup>+</sup> ion irradiation causes the RBM signals to weaken.

Similar modification on the SWNTs has been studied by many researchers via electron irradiation.<sup>11–14</sup> These reports showed that electron irradiation removes carbon atoms (either ejected or as interstitials) from their lattice sites, creating structural defects in the nanotube by knock-on displacements. Due to the dangling bonds associated with the radiation-induced vacancies, nanotubes will undergo surface reconstructions of its graphene structure. In our experiment, Ga<sup>+</sup> ion irradiation was performed at lower energy (30 keV) than the energy of electron irradiation (200 keV) experiment conducted previously.<sup>11</sup> However, the rough estimate on the impact momentum of Ga<sup>+</sup> ion shows that it is 3 orders of magnitude higher than the momentum of an electron due to the heavier mass of Ga<sup>+</sup> ion. Also, the bigger size of the Ga<sup>+</sup> ion gives a much larger impact area on the nanotube structure.<sup>15</sup> Considering the above two factors, it is assumed that Ga<sup>+</sup> ions with a high impact momentum easily knock out carbon atoms from their lattice sites and induces structural defects along the nanotubes structure.<sup>16</sup> Also, as the number of Ga<sup>+</sup> ion scans increases, more carbon atoms will be



**Figure 4.** Micro-Raman spectra (using 785 nm wavelength laser probe) taken from different positions on the Si pillar samples by scanning the laser beam along the line A–B (the brighter path in the optical microscope image shows selectively  $\text{Ga}^+$  ion irradiated region). (a) Spectral range between 1200 and 1700  $\text{cm}^{-1}$  where G-bands and D-bands are observed. (b) The low-frequency range of the Raman spectra at the RBM region.

gradually removed from nanotube lattices. Therefore, it may be suggested that the continuous straightening of suspended SWNTs occurs during ion irradiation to lower the high-energy state of the defective and curved nanotubes; straightening occurs due to the loss of mass through carbon atom

removal via pathways that lead to saturation and rehybridization of carbon bonds near vacancy positions, as postulated during electron irradiation experiments.

In conclusion, we have demonstrated that straightening and selective removal of SWNTs can be achieved using  $\text{Ga}^+$

ion irradiation in a focused ion beam (FIB) system. This can be used to produce large area networks of straight, well-ordered nanotubes. Although Ga<sup>+</sup> ion irradiation induces structural defects into the as-grown suspended nanotubes, the self-assembled nanotube networks on designed patterned substrates remain close to that of the originally grown structures. The technique described here will enable further control in the fabrication of ordered SWNT based systems for various applications.

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