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Bottom-up sample preparation technique for interfacial characterization of vertically aligned carbon nanofibers

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Abstract

We propose a novel technique for characterizing interfacial structures in vertically aligned carbon nanofibers (CNFs) utilizing scanning transmission electron microscopy (STEM). In this technique, vertically aligned CNFs are selectively grown using plasma-enhanced chemical vapor deposition (PECVD), on a substrate comprising a narrow strip (width ~100 nm) formed by focused ion beam. Using STEM, we obtain images of nanostructures of CNFs having diameters as small as 10 nm, while focusing on the interfacial region near the nanofiber base. Stacked graphite sheets parallel to the substrate are observed near the base of these CNFs.

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Keywords: Carbon nanofiber; Interconnect; Sample preparation; Focused ion beam (FIB); Scanning transmission electron microscopy (STEM)

1. Introduction

Vertically aligned carbon nanofibers (CNFs) grown by plasma-enhanced chemical vapor deposition (PECVD) have been introduced for various applications [1–3]. For future integrated devices, a "bottom-up approach" for electrical interconnects using CNFs has been proposed [4,5]. For successful implementation of CNFs as on-chip electrical interconnect materials, the detailed nanostructures of CNFs must be understood since they determine electrical transport properties. The various nanostructures of the CNF body such as "stacked cup-shaped" or "bamboo-like" features have been observed using transmission electron microscopy (TEM) [6–8]. In addition to the body of CNFs, it is also important to characterize the structure near the base of CNFs, i.e., the interface where CNFs are attached to the substrate. Previous research has shown a nanofiber with several graphitic layers lying parallel to the Si substrate [9]. In that study, CNFs with diameters of ~100 nm on planar Si substrates were examined. However, in further development for electrical interconnect applications, via sizes smaller than 100 nm in diameter are required [10]. Therefore, it is important to reveal the morphology of CNFs with diameter less than 100 nm in the CNF-metal interface region.

In order to characterize the interface structure of CNFs grown on substrates, scanning transmission electron microscopy (STEM) and TEM have been used extensively [9,11]. Focused ion beam (FIB) systems using Ga ions or ion beam milling using Ar ions have been widely employed as tools for TEM sample preparation [12,13]. In general, the thickness of the TEM sample needs to be approximately 100 nm after ion beam milling. During ion beam milling, a material that can protect CNFs from ion beam damage has to be deposited over the CNFs. A thin foil that contains CNFs is then prepared using optimized ion beam milling conditions. If the CNF diameter is 80–100 nm,

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conventional ion beam milling can be used to prepare a thin foil to be examined by TEM. However, if the CNF diameter is 50 nm or less, conventional ion beam milling is not as effective due to the following reasons. First, TEM images will be constructed by a convolution of transmitted electrons through both CNFs and the protection material over the CNFs. Secondly, the ion beam may damage the intrinsic CNF structure in the process of thinning below 100 nm because ions can scatter laterally into the thin foil [14]. In order to reduce these uncertainties associated with ion beam damage in the process of TEM sample preparation, a variety of techniques have been presented [14,15]. However, these techniques are difficult to utilize in practice because CNFs cannot be easily found in a prepared thin foil due to their small diameter, i.e., the thinner a foil, the less chance there is to find the CNFs in the foil. These issues have made the interface characterization of small-diameter CNFs exceedingly difficult.

As one of the solutions to overcome such difficulties, we propose a technique, "bottom-up" sample preparation, for the analysis of CNFs using STEM and TEM. This technique is based on the fact that CNFs are selectively grown on a substrate comprising a pre-determined narrow strip formed by FIB milling, in contrast to conventional processes in which ion beam milling is performed after the CNFs are grown and covered by a protective material, as previously reported [9,11]. In this paper, we describe our unique CNF sample preparation technique in detail. In addition, we present for the first time nanostructures of CNFs with various diameters based on detailed STEM structural analysis made possible by this newly developed sample preparation technique.

2. Sample preparation

A schematic diagram of the sample preparation procedure is shown in Fig. 1. First, a 30 nm Ti layer and a 35 nm Ni catalyst layer are deposited on a Si wafer using electron beam evaporation (Fig. 1(a)). Subsequently, a narrow strip with width of approximately 100 nm is fabricated on one of the edges of the sample (Fig. 1(b)) by locally milling the Ni, Ti, and Si using FIB (Hitachi FB-2100), as shown in Fig. 1(c). The edge of the sample is used because both the area to be milled and the time required for milling need to be minimized as much as possible in order to prevent re-deposition of Ni, Ti, and Si on the narrow strip during the milling process. In order to fabricate the narrow strip, a Ga+ ion beam with a 40 kV acceleration voltage, 10 pA ion current, and approximately 10 nm beam size is used. It is preferred that the sample is cut to 1 mm × 2 mm in order to be mounted on the STEM holder before FIB thinning, because most commercial STEM or TEM holders limit the size of bulk sample. Finally, CNFs are selectively grown on the narrow strip using PECVD with a gas mixture of NH_3:C_2H_2 (4:1) at a pressure of 4 torr during the reaction. The detailed growth conditions have been previously reported [16]. By simply mounting and tilting the sample on the STEM holder and observing from one side of the CNFs on the narrow strip (as in Fig. 1(e)), images of the nanostructures of the CNFs can be readily obtained.

3. Results and discussion

Scanning electron microscopy (SEM) images of the as-formed narrow strip before CNF growth are shown in

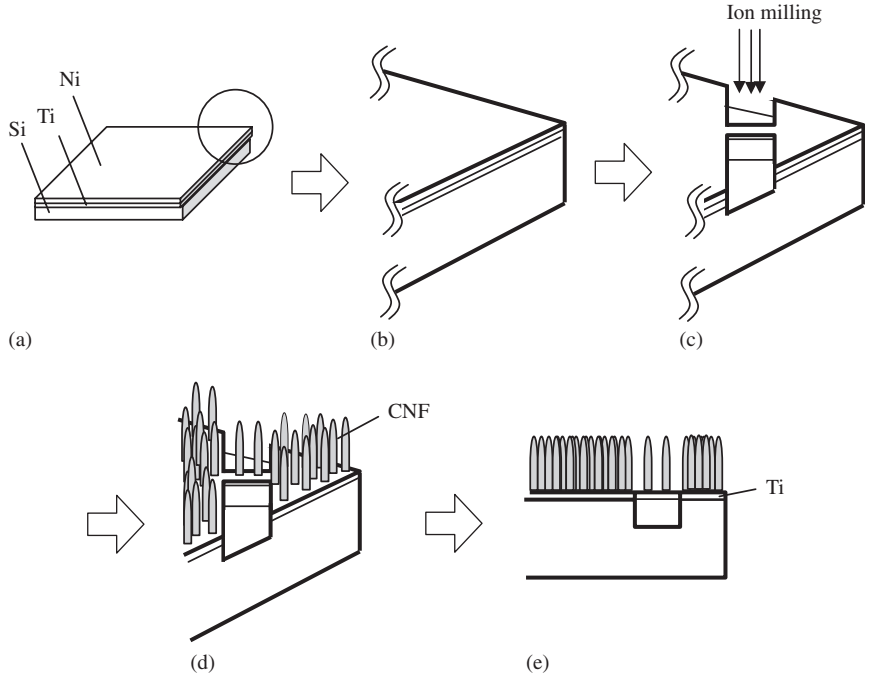

Fig. 1. Schematic diagram of the bottom-up sample preparation procedure: (a) 35 nm Ni/30 nm Ti/Si substrate; (b) the edge of the sample where ion milling is performed; (c) a narrow strip prepared by ion milling; (d) CNFs on the narrow strip, and (e) side view of CNFs on the narrow strip.

Fig. 2(a) and (b). The width of the narrow strip is approximately 100 nm (Fig. 2(a)). The Ni and Ti layers on top of the narrow strip can be observed in Fig. 2(b). The SEM images of vertically aligned CNFs on the narrow strip after CNF growth are shown in Fig. 2(c) and (d). The maximum length and density of the CNFs are approximately 2 μm and 15 CNFs/μm^2, respectively. These numbers are the same as those in the bulk region. Thermal stability of the narrow strip is inferred since no change on the strip is observed after the CNF growth. Also, the CNFs on the narrow strip exhibit identical morphology and dimensions as those grown in the bulk region of the sample.

The narrow strips before and after CNF growth are further examined by energy-dispersive X-ray spectroscopy (EDX). As shown in Fig. 3(a), the EDX mapping of the narrow strip before CNF growth indicates no substantial change in the composition of each layer during FIB milling. In the EDX mapping of the narrow strip after CNF growth, it is clearly observed that the CNFs consist

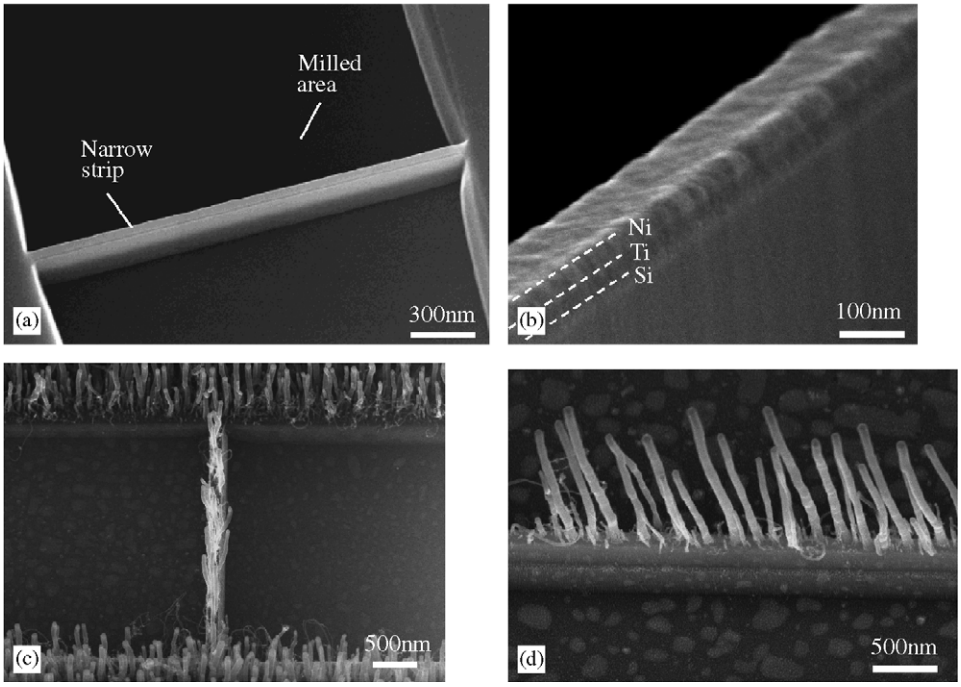

Fig. 2. SEM images of (a,b) narrow strip fabricated using FIB and (c,d) vertically grown CNFs on narrow strip.

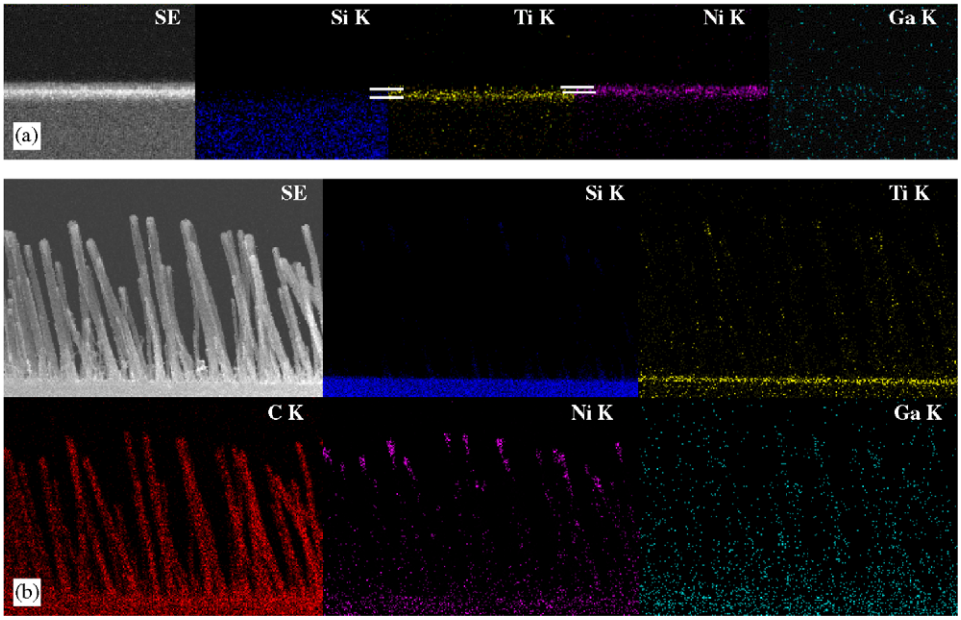

Fig. 3. EDX mapping (a) before and (b) after CNF growth on narrow strip from cross-sectional direction.

of carbon in the main body and Ni in the tip section, as shown in Fig. 3(b). The carbon detected in the Si substrate region could be attributed to signal originating from CNFs in the bulk region, or to TiC formed in the base region. In Fig. 3(a) and (b), a small Ga signal is detected in the Ni catalyst. Approximately 1 at% Ga is present in the Ni catalyst. This small quantity does not result in any differences in length, size, density, and cup-shaped structure of CNFs grown on the narrow strip, compared to those in the bulk region. Therefore, it is considered that the effect of such a small amount of Ga on CNF growth is negligible.

Cross-sectional images of CNFs covered with and without SiO_2 are observed in Fig. 4(a) and (b), respectively, using STEM (Hitachi HD-2300). The sample in Fig. 4(a) is prepared with a conventional technique (CNF-growth, SiO_2 deposition, followed by FIB thinning) [11]. The oxide is deposited using tetraethylorthosilicate (TEOS)-CVD [4].

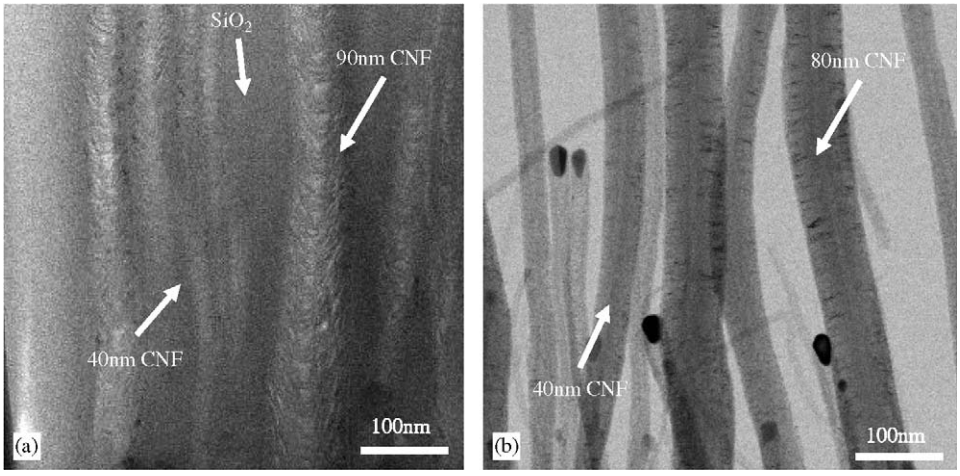

Fig. 4. STEM images of thin sample including CNFs (a) embedded with SiO_2 and (b) without SiO_2.

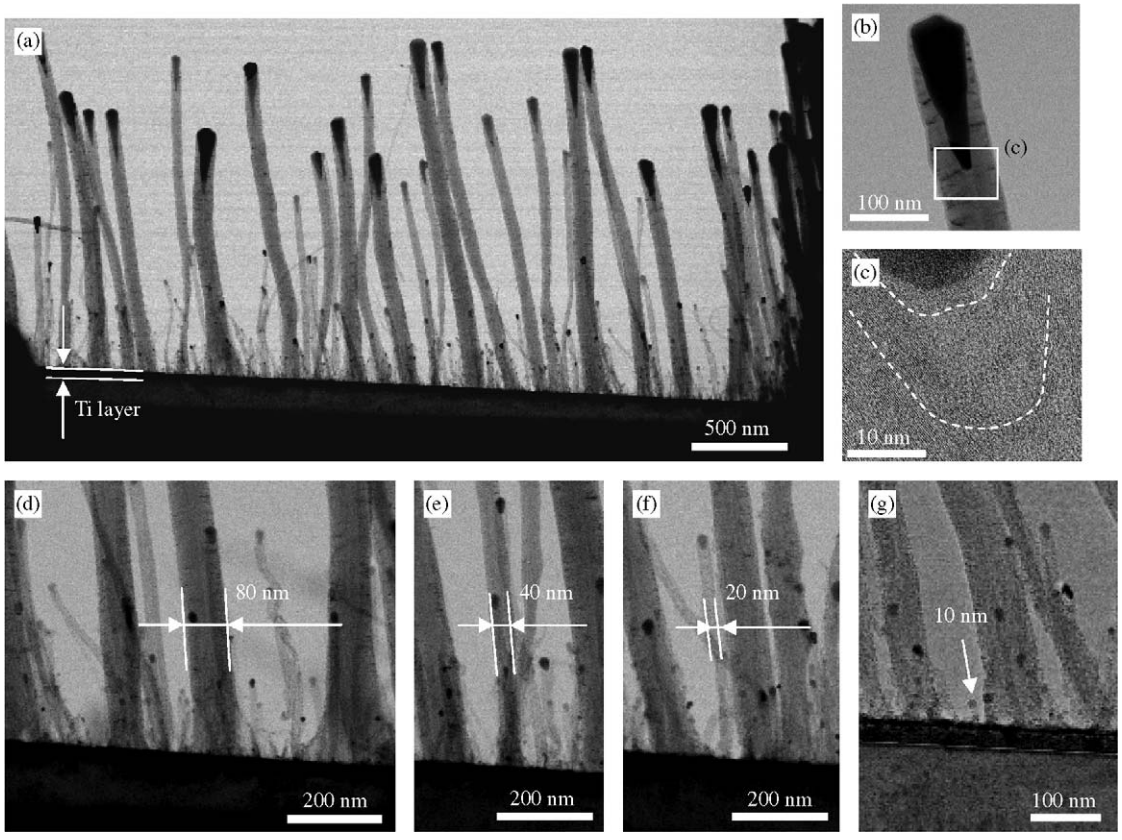

Fig. 5. STEM images of CNFs on narrow strip (a) wide view of cross-section, (b) tip, (c) the cup-shape structure at high magnification, (d) 80 nm, (d) 40 nm, (e) 20 nm, and (f) 10 nm in diameter. In (c), the broken lines indicate the graphitic layer orientations.

The thickness of the thin foil is approximately 100 nm. Although CNFs of 90 nm in diameter are clearly observed in Fig. 4(a), CNFs having diameter less than 40 nm are hardly resolved due primarily to the fact that the signal transmitted from the smaller CNFs are much less than that from larger CNFs. In contrast, the images of the CNFs in Fig. 4(b) are constructed mainly from transmitted electrons through only the CNFs. More importantly, the CNFs grown on the narrow strip are not subjected to any damage associated with ion milling because the milling is carried out before CNF growth.

The STEM images of CNFs grown on the narrow strip at low magnification are shown in Fig. 5(a)–(g). The CNFs appear to consist of a cup-shaped internal structure (Fig. 5(b) and (c)), as previously reported [5–7]. It is observed that CNFs with various diameters (e.g. 10, 20, 40, and 80 nm) have been grown on the narrow strip as shown in Fig. 5(d)–(g). This is mainly because the thin and narrow Ni layer gives rise to many catalyst particles with various diameters under the conditions of the initial CNF growth. High-magnification STEM images can reveal the detailed interfacial nanostructure of CNFs with diameters as small as 10 nm, as shown in Fig. 6(a)–(f). It is clearly observed that the base of each of these CNFs on Ti consists of stacked graphitic sheets almost parallel to the substrate. The interface structure does not seem to vary significantly with the CNF diameter. Detailed studies of the nanostructures in the interface among Ni, Ti, and CNF are in progress.

4. Conclusion

A novel bottom-up sample preparation technique for cross-sectional microscopic characterization of CNFs has been presented. Cross-sectional STEM samples are prepared by growing CNFs on a narrow strip consisting of a Ni catalyst layer and a Ti layer deposited on Si substrate. We examine the nanostructures of CNFs, with diameters ranging from 10–80 nm, near the tip and at the interface with the metal underlayer. STEM images reveal stacked graphitic sheets near the interface for all nanofibers in this size range. Our results have demonstrated that the bottom-up sample preparation technique based on the selective growth of CNFs on a pre-defined narrow strip is very useful for STEM imaging of interfacial nanostructures. This method can be readily applied to any other nano devices and materials fabricated using a bottom-up methodology [17]. We expect that new knowledge obtained from nanostructure interface images of CNFs prepared using bottom-up sample preparation will facilitate the development of on-chip CNF interconnects.

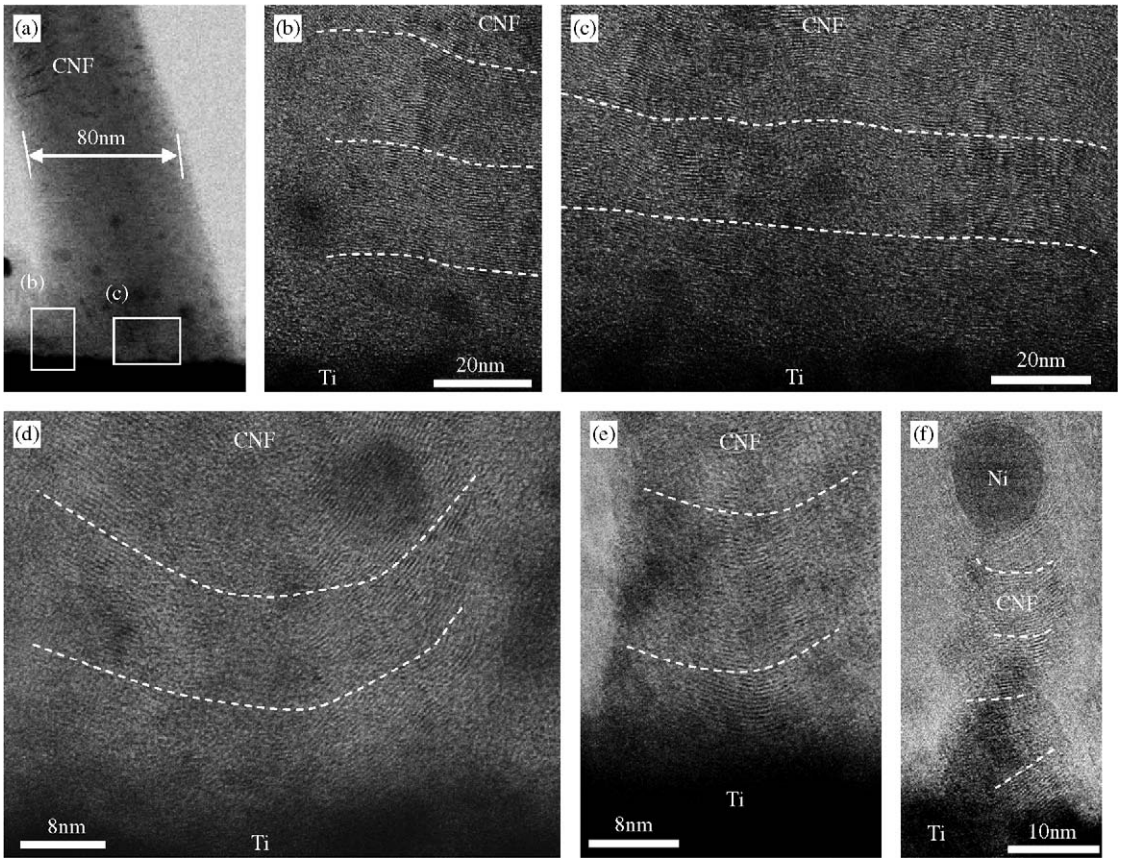

Fig. 6. STEM images of CNFs in base region: (a) 80 nm in diameter at the low magnification, (b,c) at the left edge and center of 80 nm-CNF, (d) 40 nm, (e) 20 nm, and (f) 10 nm. The broken lines indicate the graphitic layer orientations.

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