Analyses on Crystalline Structures of Carbon Nanowalls by Grazing-Incidence X-Ray Diffraction Using Synchrotron Light Source

Recently, carbon nanomaterials, such as fullerenes, carbon nanotubes (CNTs), graphene sheets, carbon nanowalls (CNWs), and so forth have attracted much attention because of their unique structures, chemical and physical strengths, and excellent electronic properties [1]. In particular, the CNWs, which are two-dimensional stacked graphene sheets vertically standing on substrates, are promising for applications in various devices, owing to their high aspect ratio, large specific surface area, high carrier mobility, and large current-carrying capability (Fig. 1). Figures 2(a) and 2(b) show top-view and cross-sectional SEM images of typical CNWs grown on a Si substrate using a C_2F_6/H_2 mixture gas plasma with O_2. We have succeeded to control the shapes and crystalline structures of CNWs using a radical injection plasma-enhanced chemical vapor deposition system (RI-PECVD) [1]. We have also reported that the crystallinity of CNWs can be improved by adding O_2 gas into the growth ambient [2]. On the other hand, the electrical properties of CNW strongly depend on their structures and crystallinity. The interfacial layer, which is grown at an initial stage of CNWs growth between the CNWs and substrates, is also essential to the crystalline structures and electrical properties of CNWs. Therefore, it is important to investigate the crystalline structures of CNWs and interfacial layers. However, it is difficult in general to evaluate the crystalline structures of nanomaterials such as CNWs using laboratory equipment, since most of them have quite low coverage and filling fraction on the substrate surfaces. Therefore, a high-resolution X-ray diffraction using a high-intensity synchrotron (SR) light source is required to evaluate the crystalline structures of carbon nanomaterials. On the other hand, grazing-incidence X-ray diffraction (GIXD) is also used to realize the substrate-insensitive measurement in this study.

In this study, the crystalline structures of CNWs were analyzed by high-resolution SR X-ray diffraction measurements with in-plane scattering geometry at beamline **BL13XU**. A multi-axis diffractometer was used in this experiment. The glancing angles of incident X-ray beams were 0.05° and 0.3°. The CNWs were fabricated using the RI-PECVD with and without the addition of O_2 gas to C_2F_6/H_2 plasma.

Figures 3(a) and 3(b) show the diffraction patterns of CNWs. In Fig 3(a), the 002 diffraction peaks of graphite are clearly observed at 16.98°. The weak 100/101, 004, and 110 peaks are also found at 27.49°, 34.16°, and 48.28°, respectively. Using Bragg's law and wavelength (λ = 0.1003 nm) of incident beam, the interlayer spacing (d_{002}) was estimated to be 0.342 nm for all the samples. This value is slightly larger than that of bulk graphite (0.335 nm) [3]. A degree of verticalness was evaluated using an intensity ratio of 002 peak to 100/101 one ($I_{002}/I_{100/101}$). It is found that the $I_{002}/I_{100/101}$ for CNWs grown without O_2 addition is twice larger than that with O_2 addition. This indicates that much more graphene sheets tilting to the substrates are included in the CNWs grown without O_2 addition, compared with those in CNWs grown with O_2 addition. Therefore, in the CNWs grown using RI-PECVD with a C_2F_6/H_2 mixture, the degree of verticalness can be

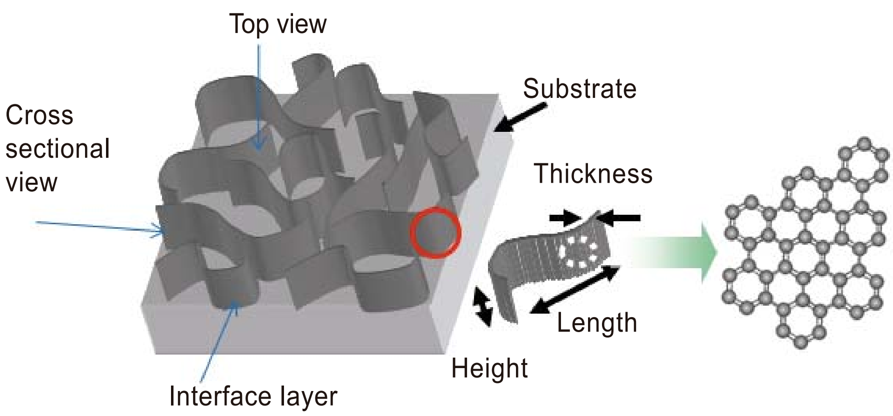

Fig. 1. Schematics of CNWs.

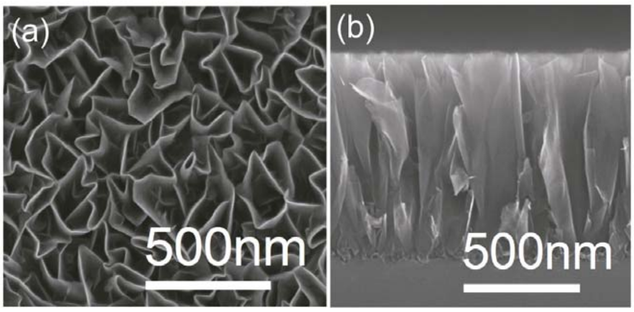

Fig. 2. **(a)** Top-view and **(b)** cross-sectional SEM images of CNWs grown on a Si substrate using a C_2F_6/H_2 mixture gas plasma with an additional O_2 gas.

improved by adding O_2 into the plasma.

In the inset of Fig 3(a), a slight and broad peak at 22.88°, which is assigned to β-SiC (111), is only observed in the absence of O_2. In Fig. 3(b), the similar peak is also found only for the glancing angle of 0.3°. Since this peak does not appear for the measurement at the glancing angle of 0.05°, it is guessed that a near-amorphous β-SiC layer exists between the CNWs and substrates. These experimental results suggest that, by employing the GIXD with the SR light source, not only the crystalline structures and orientation of carbon nanomaterials but also those of their interfacial layers can be evaluated.

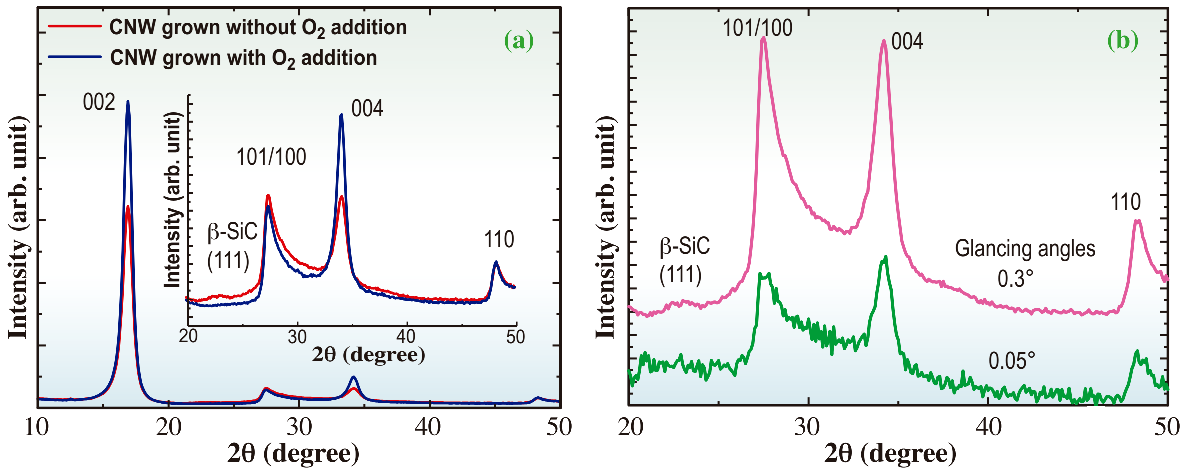

Fig. 3. X-ray diffraction (XRD) profiles of **(a)** CNWs grown with and without O_2 addition measured at a glancing angle of 0.3°, and those of **(b)** CNWs grown without O_2 addition measured at glancing angles of 0.05° and 0.3°.

Wakana Takeuchi, Hiroki Kondo and Masaru Hori*

Dept. of Electrical Engineering and Computer Science, Nagoya University

*E-mail: hori@nuee.nagoya-u.ac.jp

References

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