

## Edge Termination on Electrical Properties of Vertically-grown Graphene Sheets Employing N<sub>2</sub>/H<sub>2</sub> Mixture Plasma

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### 1. Introduction

New carbon materials, such as zero-dimensional (0D) fullerene (C<sub>60</sub>), one-dimensional (1D) carbon nanotubes (CNTs), two-dimensional (2D) graphene sheet, and so forth, have been attracting much attention from the viewpoints of both fundamental science and potential applications to nanotechnology devices. One of the main interests is the variety of their physical and chemical features depending on unique morphology. Especially, a graphene sheets has many advantages. It is well-known that electron mobility in graphene sheet is 10000-15000 cm<sup>2</sup>Vs<sup>-1</sup> [1]. Furthermore, although the graphene sheet is intrinsically zero energy bandgap semimetal, chemical terminations of graphene edges could induce generation of energy bandgap [2, 3]. Therefore, the graphene sheets are one of the hottest materials for the next generation nanoelectronics, and the chemical termination of graphene edge is essential to control their electrical properties. In recent years, we focused on carbon nanowalls (CNWs), which are one of the carbon nanomaterials consist of stacks of graphene sheets standing vertically on substrate. We have developed an innovative plasma-enhanced chemical vapor deposition system with radical injection (RI-PECVD) and have established highly reliable growth processes for CNWs and techniques for controlling their morphologies and electrical properties by controlling radicals in the plasma [4]. As a result, we found that the electrical conductivities of CNWs are temperature dependent, which indicates semiconducting behavior and that they can be controlled by the addition of molecular nitrogen gas during the growth process. These results indicate the potential to develop devices based on CNWs and thus have attracted much interest. Very recently, we have investigated the electrical properties of CNWs synthesized using CH<sub>4</sub>/H<sub>2</sub> plasma, and reported the slight thermally-activated behavior of the CNWs with no impurity [5]. In this work, we investigated the effect of edge termination of CNWs on their crystallographic and electrical properties. After the syntheses of the CNWs by the CH<sub>4</sub>/H<sub>2</sub> plasma, the post-synthesis treatments employing N<sub>2</sub>/H<sub>2</sub> and N<sub>2</sub> plasma, and NH<sub>3</sub> solution. The morphology, crystallinity, and conductivity of the treated CNWs were investigated.

### 2. Experimental

The CNWs films were synthesized by the RI-PECVD. The RI-PECVD was the high frequency (VHF) plasma-enhanced CVD system with H radical injection. This system consists of a parallel-plate VHF (100 MHz) capacitively coupled plasma (CCP) region and a surface wave microwave (2.45 GHz) excited H<sub>2</sub> plasma (H<sub>2</sub> SWP) region as a radical source. A carbon source gas (CH<sub>4</sub>) was introduced into the VHF CCP region. During the CNWs synthesis, the SiO<sub>2</sub> substrate was heated using a carbon heater. The flow rates of CH<sub>4</sub> and H<sub>2</sub> were maintained at 100 and 50 sccm, respectively and working pressure was 1 Pa. The substrate temperature was 600°C and the VHF power was 400 W. Heights of all films are maintained to be 1,000±100 nm. After the synthesis, the H<sub>2</sub>/N<sub>2</sub> plasma generated at the CCP region were exposed to the some samples. Mixture ratios of N<sub>2</sub> to H<sub>2</sub> (N<sub>2</sub>:H<sub>2</sub>) are 1:3 (N<sub>2</sub>: 25%), 1:1 (N<sub>2</sub>: 50%), 3:1 (N<sub>2</sub>: 75%). N<sub>2</sub> plasma (N<sub>2</sub>: 100%) was also performed to one of the samples. Plasma treatment times were 30 s. Furthermore, diluted NH<sub>3</sub> solution treatment for 4 hours was also used for comparison.

### 3. Results and discussions

Optical emission spectra of CH<sub>4</sub>/H<sub>2</sub>, N<sub>2</sub>/H<sub>2</sub> and N<sub>2</sub> plasmas during the CNW synthesis and the post-synthesis plasma treatment are shown in Figure 1. In the OES spectrum during the synthesis, the main emission peaks correspond to the CH at 432 nm (A<sup>2</sup>Δ-X<sup>2</sup>Π), the hydrogen lines H<sub>α</sub> at 656 nm, and H<sub>β</sub> at 487 nm, respectively. Numerous H<sub>2</sub> molecular bands are also visible, particularly centered at 602 nm. In the OES spectrum during the N<sub>2</sub>/H<sub>2</sub> and N<sub>2</sub> plasma treatments, a variety of nitrogen emission peaks appeared. The four bands in the visible region, with band heads at approximately 540, 580, 650, and 750 nm, are commonly associated with the first positive system of N<sub>2</sub> (B<sup>3</sup>Π<sub>g</sub>-A<sup>3</sup>Σ<sub>u</sub>), these are thought to occur as a result of the recombination of ground-state nitrogen. And, CN peak also appeared in the case of the N<sub>2</sub>/H<sub>2</sub> plasma. It is found that intensities of nitrogen peaks increases with increasing the N<sub>2</sub> mixture ratios.

Figures 2 (a) ~ (f) are cross-sectional SEM images of the CNWs grown on SiO<sub>2</sub> substrates. The heights of CNWs were about 1,000±100 nm. After the plasma treatment, the sides of CNWs became rough slightly, although that hardly

changed by the  $\text{NH}_3$  treatment. Figure 3 (a) shows the Raman spectra of the CNWs before and after the post-synthesis treatments. They reveal a typical spectrum of nanocrystalline graphitized structure with a G-band peak at  $1580\text{ cm}^{-1}$  and D-band peak at  $1350\text{ cm}^{-1}$ , which corresponds to the six-membered ring structures in graphene and the disorder-induced phonon mode, respectively. Additionally, the G-band peak is accompanied by a shoulder peak (D'-band peak) at  $1620\text{ cm}^{-1}$ , which is related with the limited-size graphite crystallites and graphene edges. The 2D peak at  $2680\text{ cm}^{-1}$  is a signature of graphitic carbon in the graphene-like materials. The disorder-induced combination mode (D+G peak) at  $2940\text{ cm}^{-1}$  was also observed. The small 2D' peak at  $3230\text{ cm}^{-1}$  is attributed to the structural disorder in the CNWs. The decreased intensity of the D band in the Raman spectra of graphite has been interpreted as decrease in effects of edges. Figure 3 (b) shows the intensity ratio of D-band peak to G-band peak ( $I_D/I_G$ ) and G-band peak full-width half maximum (FWHM) after the post-synthesis treatment. The  $I_D/I_G$  value slightly decreased after the  $\text{NH}_3$  solution treatment, and further decreased by the  $\text{N}_2/\text{H}_2$  and  $\text{N}_2$  plasma treatments. With increasing  $\text{N}_2$  mixture ratio, the  $I_D/I_G$  value decreased. The Raman features of N-containing films are generally explained as due to the substitution of C atoms in the graphitic clusters by N atoms, which break the long-range order of the graphitic structure and promote the clustering of  $\text{sp}^2$  sites. In Fig. 3, the  $I_D/I_G$  ratio and FWHM value of G-band peak show the opposite trend; the  $I_D/I_G$  ratio decreases and FWHM value of G-band peak increases with increasing the  $\text{N}_2$  mixture ratio. It is suggested that substitution and edge termination by nitrogen simultaneously occurred [6].

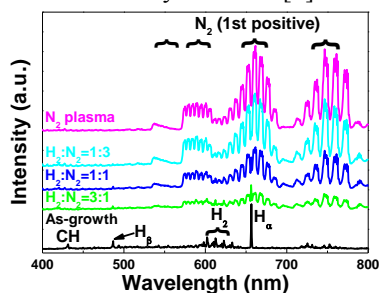


Fig. 1 Optical emission spectra of  $\text{CH}_4/\text{H}_2$ ,  $\text{H}_2/\text{N}_2$ , and  $\text{N}_2$  plasmas during the synthesis and the post-synthesis plasma treatment.

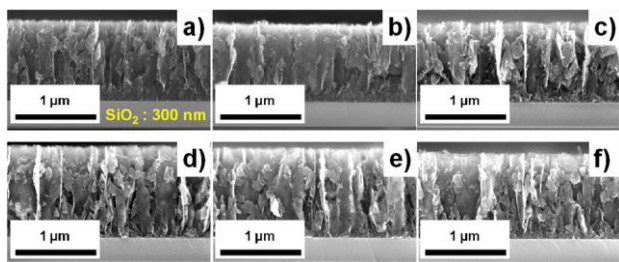


Fig. 2 Cross-sectional SEM images of the CNWs before and after the post-synthesis treatments.

Figure 4 is the electrical conductivity of CNWs and before and after the post-synthesis treatments. The conduc-

tivity decreased with increasing  $\text{N}_2$  mixture ratio. This means the nitrogen incorporation would induce carrier generation.

### 3. Conclusions

Effects of  $\text{NH}_3$  solution,  $\text{H}_2/\text{N}_2$ , and  $\text{N}_2$  mixture plasma treatment on crystallographic and electrical properties of the CNWs were investigated. In the Raman spectra, relative intensity of D-band peaks and FWHM value of G-band peak indicated opposite trend. These results suggested that substitution and edge termination by nitrogen simultaneously occurred and induced complicated change in crystallinity. The electrical conductivity decreased with increasing  $\text{N}_2$  mixture ratio. This means the nitrogen incorporation would induce carrier generation. The knowledge obtained in this study will open the way to control electrical properties of the vertically-grown graphene sheets and advanced application of CNWs.

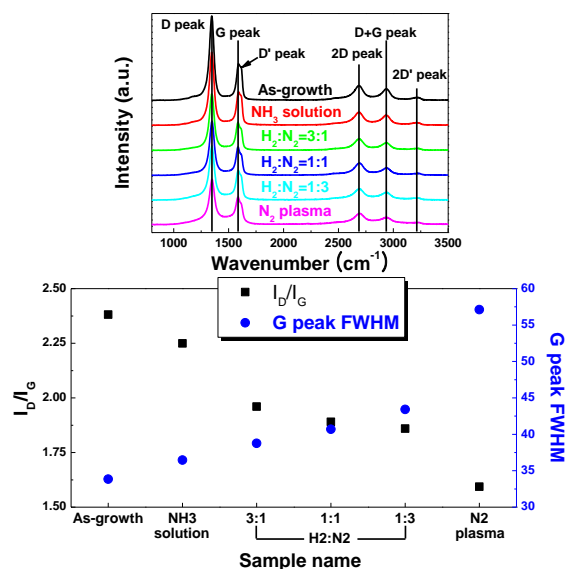


Fig. 3 (a) Raman spectra of CNWs and, (b)  $I_D/I_G$  ratio and FWHM value of G-band peak before and after the post-synthesis treatments.

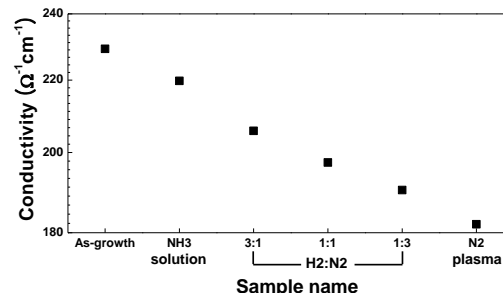


Fig. 4 Conductivity of CNWs before and after the post-synthesis treatments.

### References

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