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Crystallographic and Electrical Properties of Semiconducting Graphene Nanoribbon Grown Employing CH_4/H_2 plasma

Hyung Jun Cho, Keigo Takeda, Hiroki Kondo, Kenji Ishikawa, Makoto Sekine and Masaru Hori

Nagoya Univ.
Department of Electrical Engineering and Computer Science,
Furo-cho, Chikusa-ku, Nagoya, Aichi 464-8603, Japan
Phone: +81-52-789-3461 E-mail: cho.hyung.joon@g.mbox.nagoya-u.ac.jp

1. Introduction

New materials composed of carbon atoms have been attracting much attention from the points of view of both fundamental science and potential applications to nanotechnology devices. One of the main interests is the variety of their physical and chemical natures depending on geometries. Especially, a graphene nanoribbon has many advantages. It is well-known that the graphene nanoribbon has small amount of energy bandgap in its electronic structure, and chemical terminations of nanoribbon edges induce increase in energy bandgap [1, 2]. Therefore, the graphene nanoribbon is one of the hottest materials for the next generation nanoelectronics.

In recent years, we focused on carbon nanowalls (CNWs), which is one of the carbon nanomaterials consist of graphene sheets [3, 4]. Figure 1 shows an SEM image of typical CNWs [5]. In this figure, a peeling part of CNWs is found and looks like a wavy nanoribbon. Therefore, the CNWs can be considered as an assembly consisting of free-standing graphene nanoribbons. Such the free-standing graphene nanoribbons are promising materials applied to the novel electronic devices. In addition to such the unique morphology, the CNWs have fine field-emission and charge transport properties [4]. Recently, we have reported semiconducting behaviors of the CNWs synthesized by radical-injection plasma-enhanced chemical vapor deposition (RI-PECVD) employing C_2F_6/H_2 plasma [6]. Such the semiconducting behaviors are attributed to incorporated fluorine (F) atoms, or fluctuations of crystalline structures, such as bending and branching structures, defects and edges of graphenes, so forth. However, details of its mechanisms are not clear yet.

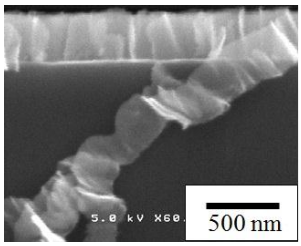

Fig. 1 SEM images of nano graphene ribbons with unique substrate [5].

In this work, we synthesized the CNWs by the RI-PECVD using CH_4/H_2 plasma. Since the CNWs synthesized in this experiment have no F atoms in themselves, effects of structural fluctuations on electrical properties can be discussed.

2. Experiments and results

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_2 plasma (H_2 SWP) region as a radical source. A carbon source gas (CH_4) was introduced into the VHF CCP region. During the CNWs synthesis, the SiO_2 substrate was heated using a carbon heater. The flow rates of CH_4 and H_2 were maintained at 100 and 50 sccm, respectively. The substrate temperature was 600^{o}C and the VHF power was 300 W. In this study, CNWs films were synthesized at various total pressures ranging from 1 to 5 Pa. Heights of all films are maintained to be 500±40 nm. The plasma diagnostics were measured by optical emission spectrometry (OES). Scanning electron microscopy (SEM) was used to evaluate the surface morphology of the CNWs. Raman spectroscopy was used to determine the crystallinity of CNWs films. The electrical conductivity of the CNWs films were measured at temperatures ranging from 80 to 300 K.

Figure 2 shows peak intensity ratios of H_α to CH (H_α : 658.0 nm / CH : 432.6 nm) in OES spectra as a function of total pressure. Typical OES spectrum obtained at a total pressure of 5 Pa were also shown in inset. As shown in the figure, with increasing the total pressure, H_α/CH value increases. This indicates that the relative density of H radicals increases with total pressures.

Figures 3 (a), (b) and (c) are top-view and cross-sectional view SEM images of the CNWs grown on SiO_2 substrates at total pressures of 1, 3 and 5 Pa, respectively. Characteristic morphologies of CNWs are found in all images. The thickness of CNWs was approximately 10 nm, and their heights were about 500±40 nm. It was found that the density of CNWs decreased with increasing the total pressure. Similar behaviors have been obtained in the case of CNWs synthesized employing C_2F_6/H_2 plasma [4]. Etching effects owing to H radicals result in decrease in density of CNWs. Figure 4 shows the Raman spectroscopy of the CNWs. They reveal a typical spectrum of nanocrys-

talline graphitized structure with a G-peak at 1580 cm^{-1} and D peak at 1350 cm^{-1}, which corresponds to the six-membered ring structures in graphene and the disorder-induced phonon mode, respectively. Additionally, the G peak is accompanied by a shoulder peak (D'-peak) at 1620 cm^{-1}, which is related with the limited-size graphite crystalites and graphene edges. As shown in the figure, intensity ratio of D-peak to G-peak decreases with increasing total pressure. This means decrease in defect density of the CNWs.

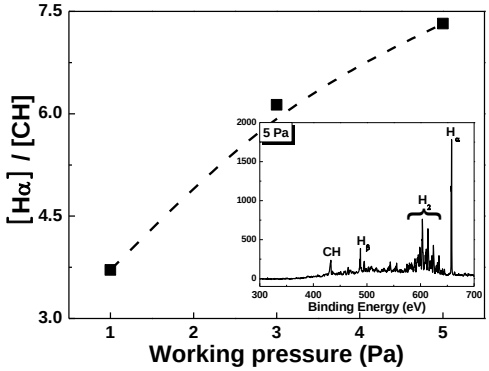

Fig. 2 Peak intensity ratios of H_α to CH in OES spectra as a function of total pressure. Typical OES spectrum obtained at a total pressure of 5 Pa is also shown in inset.

Figure 5 is the Arrhenius plot of electrical conductivity of the CNWs synthesized at 5 Pa. The electrical conductivity decreases with decreasing the measurement temperature and the activation energy (E_a) was evaluated about 9 meV. This means that the CNWs synthesized using CH_4/H_2 plasma has semiconducting property, although there is almost no impurity atom such as F in them. Therefore, from this result, it is indicated that structural fluctuations such as bending and branching structures, defects and edges of graphenes can induce semiconducting electronic structures such as energy bandgap in the CNWs. On the other hand, the obtained value of E_a, which would correspond to energy bandgap, is much smaller compared with that of the CNW synthesized using C_2F_6/H_2 plasma [6]. Therefore, it is suggested that incorporation of impurity atoms such as F is a strong inducing factor of semiconducting properties of the CNWs. These unique electrical properties of the CNWs are interesting as the characteristics of the vertically-growth graphene nanoribbons. Dependence of electrical properties of the CNWs on total pressure will also be discussed at the conference.

3. Conclusions

Crystallographic and electrical properties of the CNWs synthesized by the RI-PECVD method using CH_4/H_2 plasma were investigated. The density of CNWs decreased with increasing total pressure, resulting from increase of H radical density. Raman spectroscopy results also reveal increase of crystallinity of CNWs with total pressure. Temperature dependence of electrical conductivity of CNWs grown employing CH_4/H_2 plasma indicated a semiconducting behavior. This result indicates that structural fluctuations of stacked graphene sheets in the CNWs, such as bending and branching structures, defects and edges of graphenes, can contribute to generation of semiconducting electronic properties of the CNWs. Fine structures of CNWs can be precisely controlled by radicals or ions and the energy density in the plasma, which can be controlled by the RI-PECVD system. Therefore, the precision control of plasma realizes control of morphologies and electrical properties of CNWs.

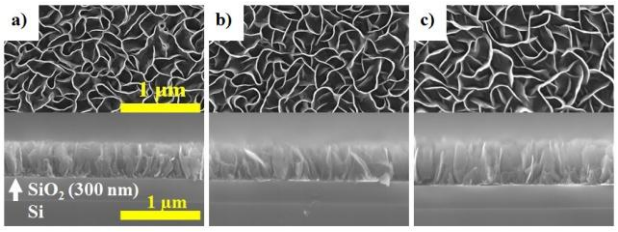

Fig. 3 Topography and cross-sectional view SEM images CNWs grown employing CH_4/H_2 plasma with different working pressure a) 1 Pa, b) 3 Pa and c) 5 Pa.

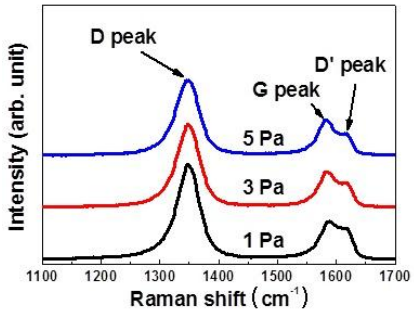

Fig. 4 Raman spectra of CNWs synthesized at total pressures of 1, 3, and 5 Pa.

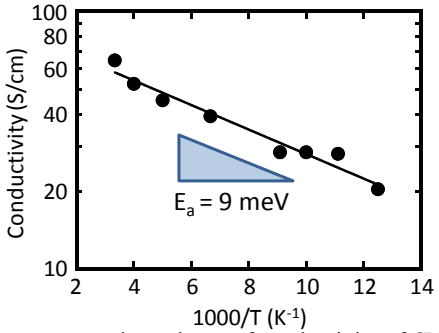

Fig. 5 Temperature dependence of conductivity of CNWs grown employing CH_4/H_2 plasma.

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