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Crystalline Structures and Electrical Properties of Carbon Nanowalls Grown by CH_4/H_2 plasma

CH_4/H_2プラズマを用いて成長したカーボンナノウォールの結晶構造および電気的特性

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Carbon nanowalls (CNWs) were synthesized by radical injection plasma-enhanced chemical vapor deposition (RI-PECVD) employing CH_4/H_2 plasma. In the optical emission spectra, H_α/CH value increases with increasing the VHF power. This indicates that the relative density of H radicals increases with VHF powers. On the other hand, in the Raman spectra, the peak intensity ratio of D-band to G-band decreases with increasing VHF power. The electrical conductivity of the CNWs grwon at shows thermally activated characteristic with an activation energy of about 3 meV.

1. Introduction

Carbon nanomaterials 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 promising 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]. The CNWs can be considered as an assembly consisting of free-standing graphene nanoribbons. Such the free-standing graphene nanoribbons are also 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 [5]. 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. However, detail mechanisms are not clear yet.

In this work, we synthesized the CNWs by the RI-PECVD using CH_4/H_2 plasma. The effects of structural fluctuations on electrical properties of the synthesized CNWs were investigated.

2. Experiments

The CNWs films were synthesized on SiO_2 substrates by the RI-PECVD. The RI-PECVD system consists of a parallel-plate very high frequency (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. The working pressure was maintained at 5 Pa in a gas mixture containing CH_4 (100 sccm) and H_2 (50 sccm). The substrate temperature was kept at 600^{o}C. The VHF powers were applied ranging from 200 to 400 W. Heights of all films were fixed at 500±40 nm. The plasma diagnostics were measured by optical emission spectroscopy (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.

3. Results

Figure 1 shows peak intensity ratios of H_α (657.1 nm) to CH (432.6 nm) in OES spectra as a function of VHF power. Typical OES spectrum obtained at a VHF power of 300 W were also shown in inset. As shown in the figure, with increasing the VHF power, H_α/CH value increases. This indicates that the relative density of H radicals increases with VHF powers.

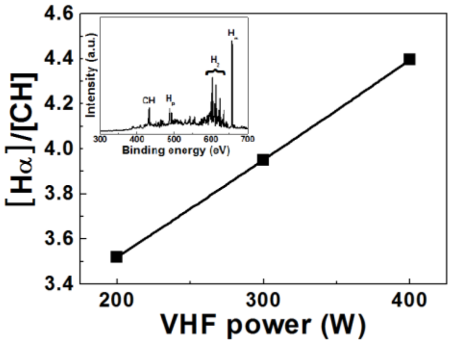

Fig. 1 Peak intensity ratios of H_α to CH in OES spectra as a function of VHF power

Figure 2 shows the Raman spectroscopy of the CNWs. They reveal a typical spectrum of nanocrystalline graphitized structure with a G-band peak at 1580 cm^{-1} and D-band one 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 leaded by a shoulder peak (D'-band) at 1620 cm^{-1}, which is related with the limited-size graphite crystallites and graphene edges. As shown in the figure, intensity ratio of D-peak to G-peak slightly decreases with increasing VHF power. This means decrease in defect density of the CNWs.

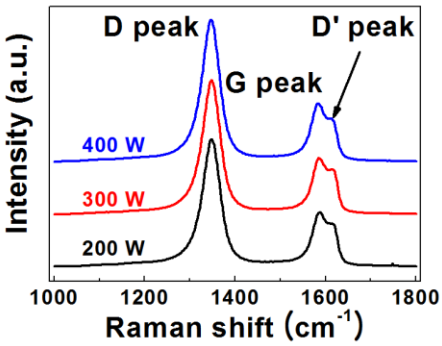

Fig. 2 Raman spectra of CNWs synthesized at VHF power of 200, 300, and 400 W

Figure 3 is the Arrhenius plot of electrical conductivity of the CNWs synthesized at 300 W. The electrical conductivity decreases with decreasing the measurement temperature and its activation energy (E_a) was evaluated about 3 meV. This means that the CNWs synthesized using CH_4/H_2 plasma has semiconducting properties although there is almost no impurity atom such as F in them. Therefore, from this result, it is deduced 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 [5]. Therefore, it suggests 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.

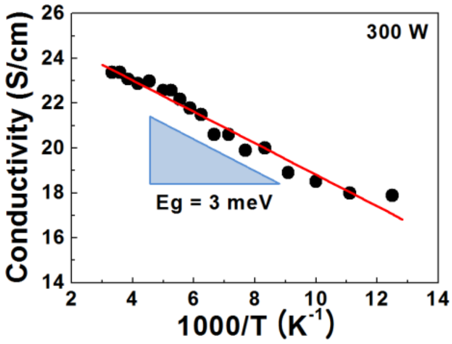

Fig. 3 Temperature dependence of conductivity of CNWs grown at 600°C.

4. 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 VHF power, resulting from increase of H radical density. Raman spectroscopy results also reveal increase of crystallinity of CNWs with VHF power. The semiconducting behavior was generated by the structural fluctuations of stacked graphene sheets in the CNWs, such as bending and branching structures, defects and edges of graphenes. Fine structures and electrical properties of CNWs can be precisely controlled by radicals and ions, and the energy density in the plasma.

References

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