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Control of Electric Conduction of Carbon Nanowalls

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1. Introduction

Carbon nanowalls (CNWs) [1], two-dimensional carbon nanostructure consisting of graphite sheets standing vertically on the substrate, have attracted much attention for several applications, including field emitter arrays, gas storage, and membranes for electrochemical energy storage. Recently, it was reported that two-dimensional multilayer graphene sheet offers high mobility and huge sustainable currents [2]. CNW films potentially would possess high mobility and huge sustainable current density since the CNWs are basically graphene sheets. Previously, we have successfully fabricated CNWs by the radio frequency plasma enhanced CVD (rf-PECVD) assisted with H radical injection [3]. Considering the practical applications of CNWs, further investigations are required to clarify the growth mechanism and to control their structure and properties. In particular, control of their electronic properties such as resistivity and conduction type is very important for obtaining the optimum advantage of CNWs. Main focus of this work is to evaluate and control the electrical properties of CNWs. We have investigated the effect of N_2 or O_2 addition to process gas mixture (C_2F_6/H_2) on the morphology and electrical properties of CNWs grown by PECVD employing fluorocarbon/hydrogen system.

2. Experiments

CNWs were fabricated by the PECVD with radical injection employing a mixture of C_2F_6 and H_2. Fig. 1 shows a schematic of the tandem type PECVD with H radical injection, which was developed for the large-area growth of CNWs with reasonable growth rate. This system consists of a parallel-plate VHF (100 MHz) capacitively coupled plasma (CCP) region and a surface wave-excited microwave H_2 plasma (H_2 SWP) as a remote H radical source. A carbon source gas (C_2F_6) was introduced into the CCP region. The heated substrate was showered with fluorocarbon radicals as well as plenty of H atoms. The flow rates of C_2F_6 and H_2 were kept at 50 and 100 sccm, respectively, and the total gas pressure was 1 Torr. Additional gas (N_2 or O_2) was introduced into the CCP region at a flow rate of 0–10 sccm.

Insulating quartz substrate was used to evaluate the electrical properties of CNWs. After synthesis of CNW film on the quartz substrate, aluminum (Al) contacts were formed at the corners on the surface of CNW film by an electron-beam evaporation. Four Al contacts were symmetrically located on the CNW film for the Hall measurement by the van der Pauw method [4]. In this measurement, it is assumed that the CNW film is a plane membrane from a macroscopic standpoint and current flows uniformly along the surface between contacts.

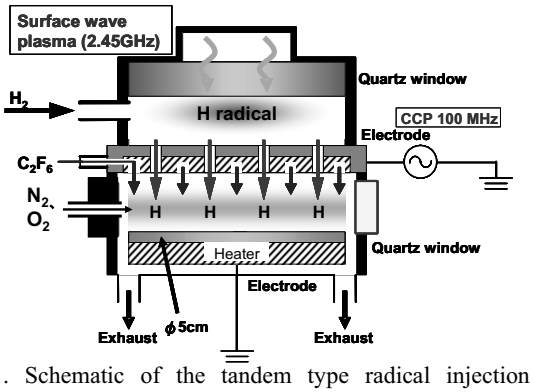

Fig.1. Schematic of the tandem type radical injection PECVD apparatus.

3. Results and Discussion

Figs. 2(a) and 2(b) show typical scanning electron microscopy (SEM) images of the CNW film grown for 30 min employing C_2F_6/H_2 system. Figs. 2(c) and 2(d) show SEM images of the CNW films grown with the addition of N_2 and O_2, respectively. As a result, N_2 addition into C_2F_6/H_2 system, the size of individual CNWs decreased and the density of CNWs increased, while the height of CNWs (thickness of CNW film) was not changed. In the case of O_2 addition, on the other hand, the growth rate of CNW film decreased drastically and the density of CNWs decreased. It is noted that definite CNWs were synthesized and the size of individual CNWs increased as a result of O_2 addition.

Hall measurements were carried out for the CNW films grown with the addition of N_2 or O_2 at different flow rates. Thicknesses of CNW films were made uniform by changing the growth time according to the growth rate. Fig. 3(a) shows the Hall coefficient of CNW film grown with the

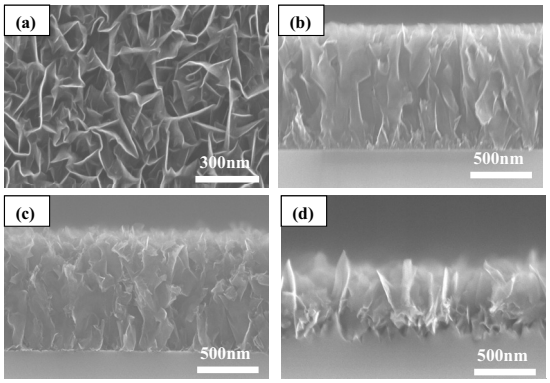

Fig.2 Typical SEM images of CNW films. (a)Top view and (b)cross-sectional view of CNWs grown employing C_2F_6/H_2 system. (c) and (d) Cross-sectional view of CNWs grown with N_2 and O_2 addition, respectively.

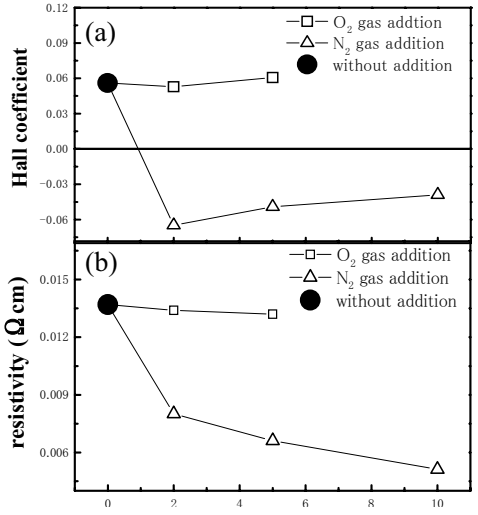

Fig. 3 (a) Hall coefficient and (b) resistivity of CNW films grown with N_2 or O_2 addition as a function of flow rate of additive.

additives at different flow rates. The Hall coefficient was positive for the CNW film grown without additives. When O_2 was added to the C_2F_6/H_2 plasma, the Hall coeffiicient was still positive and almost the same as that for the sample grown without additives. On the other hand, the Hall coeffiicient of CNW film displayed negative value when N_2 was added to the C_2F_6/H_2 plasma. The positive or negative value of the Hall coefficient implies p- or n-type, respectively. Result in Fig. 3(a) suggests that nitrogen is included in CNWs and acts as a donar.

Resistivity variation of CNW films grown with the addition of N_2 or O_2 at different flow rates is shown in Fig. 3(b). The resistivity of CNW films grown with O_2 addition was almost constant with the increase of O_2 gas flow rate. In the case of CNW film grown with N_2 addition, on the other hand, the resistivity decreased drastically at first. With further increase of N_2 addition to the C_2F_6/H_2 plasma, the resistivity of CNW film decreased gradually.

CNW films were characterized by Raman spectroscopy to evaluate the influence of gas addition on the structural property of CNWs. Raman spectra were measured using a

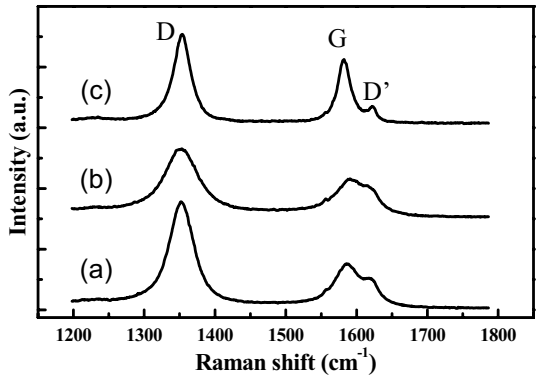

Fig.4 Raman spectra of the CNWs grown from (a) C_2F_6/H_2, (b) $C_2F_6/H_2/N_2$, and (c) $C_2F_6/H_2/O_2$,

514.5 nm line of an Ar laser. Fig. 4 shows the Raman spectra of CNW films grown with and without additives. As shown in Fig. 4, Raman spectra for CNWs are found to have G band peak at 1590 cm^{-1} indicating the formation of a graphitized structure, and D band peak at 1350 cm^{-1} corresponding to the disorder-induced phonon mode. The G band peak is accompanied by a shoulder peak at 1620 cm^{-1} (D' band). This shoulder peak is associated with finite-size graphite crystals. The strong D band peak and D' band peak suggest a more nanocrystalline structure and presence of graphene edges and defects, which are prevalent features of CNWs. As a result of O_2 addition to the C_2F_6/H_2 plasma, the peak intensity ratio of D band to G band (I_D/I_G) and G-band width decreased, as can be seen from the Raman spectrum (c). This indicates that oxygen would play a role of etching of amorphous carbon content and contribute to the higher graphitization, while conduction type of CNW films would not change by the O_2 addition. On the other hand, in the case of N_2 addition to the C_2F_6/H_2 plasma, G-band peak in the Raman spectrum (b) was broadened, indicating the slight degradation of graphite crystallinity probably due to the inclusion of nitrogen in CNWs.

4. Conclusions

CNWs were fabricated by the PECVD with radical injection employing a mixture of C_2F_6 and H_2. The effect of N_2 or O_2 addition to C_2F_6/H_2 plasma on the morphology and electrical properties of CNWs was investigated. It was found that the conduction type of CNW films was controllable by adding N_2 or O_2 to the C_2F_6/H_2 plasma. Morphology and crystallinity of CNWs were changed by the addition of N_2 and O_2. Oxygen would play a role of etching of amorphous carbon content and contribute to the higher graphitization, while conduction type of CNW films would not change. On the other hand, nitrogen would be included in CNWs and act as a donar, while accomapnied by the slight degradation of graphite crystallinity.

References

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