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Electronic Structure of Carbon Nanowalls Using Resonant Soft-X-Ray Emission Spectroscopy

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1. Introduction

Recently, several reports have been published on the growth of carbon nanowalls (CNWs), which are 2D carbon nanostructures comprising of planar graphene layers standing almost vertically on a substrate [1-3]. Since CNWs essentially consist of graphene sheets, they are expected to have high mobilities and large sustainable current densities. Therefore, CNWs are considered to be one of the most promising carbon materials for nanoscale electronic devices. In order to fully exploit the potential of graphene and to develop next-generation electronic devices, CNWs with high crystallinity are required and it is indispensable to know the electronic structure of CNWs.

In this study, CNW films were fabricated using plasma-enhanced chemical vapor deposition (PECVD) employing a C_2F_6/H_2 system with O_2 gas addition. We investigated the electronic structure of CNW films with high crystallinity.

2. Experimental

CNW films were fabricated using PECVD with H radical injection with a mixture of C_2F_6 and H_2. Details of the radical-injection PECVD system are provided elsewhere [4-5]. The C_2F_6 and H_2 flow rates were maintained at 50 and 100 SCCM, respectively. O_2 was introduced into the capacitively coupled plasma (CCP) region at flow rates of 0–5 sccm and the total pressure was maintained at 160 Pa. 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 [6]. 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.

Soft-X-ray emission spectroscopy (SXES) has long been recognized as a technique with unique capabilities as a probe of electronic structure. The electronic structure of CNWs was analyzed using synchrotron soft X-ray at the beamline BL27SU of SPring-8 [7].

3. Results and Discussion

Figure 1(a) and 1(b) shows SEM images of typical CNW film grown on a Si substrate using a C_2F_6/H_2 mixture without and with O_2, respectively, and the insets show top-view SEM images of the same CNW films. CNWs grown with O_2 addition exhibit less branching than those produced without O_2 so that monolithic graphene sheets were obtained by adding O_2 to the source mixture, while the growth rate was reduced by approximately 33%. TEM images of CNW films grown without and with O_2 are shown in Figs. 1(c) and 1(d), respectively. Small overlapping multi-layered graphene domains with random orientations were observed for CNWs grown without O_2 (Fig. 1(c)). In contrast, monolithic self-sustaining graphene sheets larger than 200 nm in size were clearly observed in the CNWs grown with O_2 (Fig. 1(d)). These results suggest that oxygen etches small graphitic fragments, thereby contributing to the higher graphitization and improving the crystallinity and electrical conduction to form highly oriented monolithic graphene sheets.

Figure 2 shows the resistivity variation of the CNW films as a function of temperature. The resistivity of CNW film was reduced by approximately 30% as a result of O_2 addition during the CNW growth process. The resistivity of all the CNW films decreased with an increase in the measured temperature, indicating the semiconductor behavior of the CNW films. The resistivity derived in this study reflects the electrical property of the bulk CNW film comprising the web of nanographene sheets with interspaces. This value could be useful for the design and evaluation of electronic devices using bulk CNW films.

The resonant SXES spectra obtained from CNW film grown with O_2 addition are shown in Fig. 3. These spectra show the C-K emission region as the incident photon energy (hv) is varied below and above the C-K edge, which is assumed to locate at hv=284.5 eV. The emission spectrum obtained for hv=320 eV, which is sufficiently far from the C-K edge, represents the normal or non-resonant C-K emission spectra for CNW film. This spectrum was similar to that of graphite [8]. On the other hand, the resonant emission spectra obtained at the incident photon energies

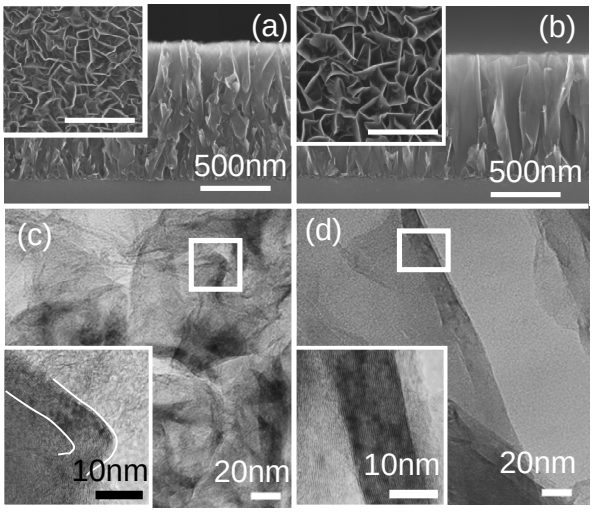

Fig. 1 Cross-sectional SEM images of (a) CNW film grown on a Si substrate using C_2F_6/H_2 and (b) CNW film grown using C_2F_6/H_2 with additional O_2 gas, together with SEM top-view images of identical CNW films as insets. TEM images of (c) CNWs grown without any additional gas and (d) CNWs grown with additional O_2, together with magnified images of square areas as insets, showing layered graphene structures of CNWs.

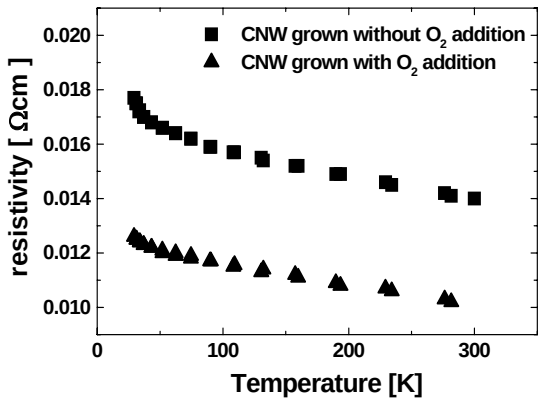

Fig. 2 Variation in resistivity of CNW films as a function of temperature.

near the C-K edge appear to change in a systematically way with excitation energy, while the shape of these spectra (A~C) was not the same as that of graphite. These features of spectra can be directly related to the band gap. Thus, it was considered that the band structure of CNW film was different from graphite. These different of the band structure would be caused that the CNW film behave as a semiconductor.

4. Conclusions

CNWs were fabricated by the PECVD with radical injection employing a mixture of C_2F_6 and H_2. The effect of O_2 addition to the C_2F_6/H_2 plasma on the morphology, electrical properties and electronic structure of CNWs was investigated. Morphology and crystallinity of CNWs were improved by the addition of O_2 during the growth process. Moreover, CNW films indicated the semiconductor behavior and the conductivity of CNW film was improved by the

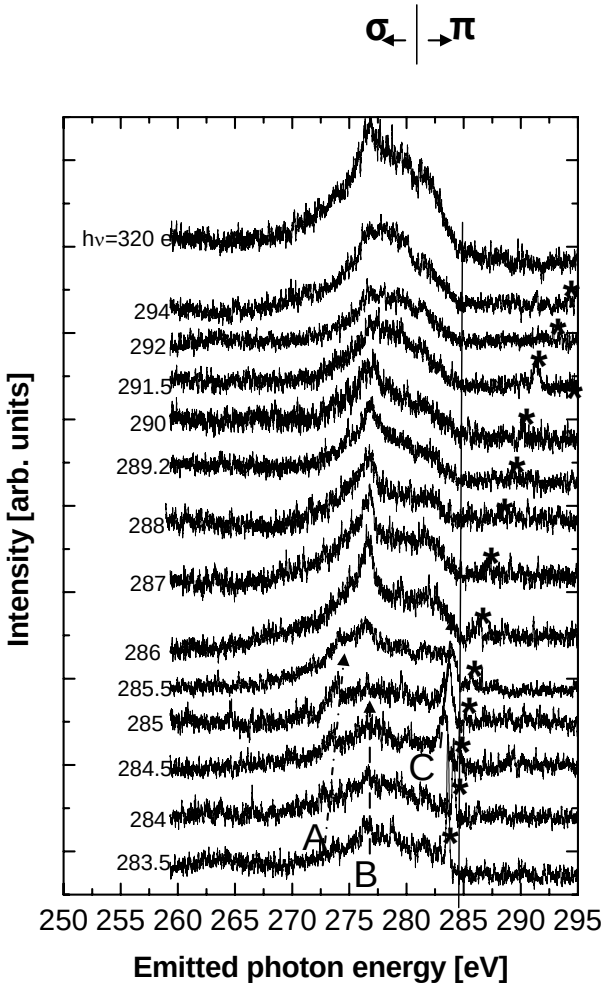

Fig. 3 Resonant emission spectra obtained from CNW film grown with O_2 gas addition to C_2F_6/H_2 plasma for incident excitation energies *hv* varying from 283.5 eV to 320 eV.

addition of O_2 during the growth process. As a result of the SXES measurement, it was found that CNWs have band structure, which was different from bulk graphite.

References

[1] Y. H.Wu, P. W. Oiao, T. C. Chong, Z. X. Shen, Adv. Mater. (Wiunheim, Ger.) **14** (2002) 64.
[2] J. J. Wang, M. Y. Zhu, R. A. Outlaw, X. Zhao, D. M. Manos, B. C. Holloway, V. P. Mammana, Appl. Phys. Lett. **85** (2004**)** 1265.
[3] M. Hiramatsu, M. Hori, Jpn. J. Appl. Phys. **45** (2006) 5522.
[4] W. Takeuchi, M. Ura, M. Hiramatsu, Y. Tokuda, H. Kano, M. Hori, Appl. Phys. Lett. **92** (2008**)** 213103.
[5] S. Kondo, M. Hori, K. Yamakawa, S. Den, H. Kano, M. Hiramatsu, J. Vac. Sci. Technol. B **26** (2008**)** 1294.
[6] L. J. Van der Pauw, Philips Technical Rev. **20** (1958) 220.
[7] T. Tokushima, Y. Harada, H. Ohashi, Y. Senba, S. Shin, Rev. Sci. Instrum. **77**, 063107 (2006).
[8] J.A. Carlisle, S.R. Blankenship, L.J. Teminello, J.J. Jia, T.A. Callctt, D.L. Ederer, R.C.C. Perera, F.J. Himpsel, Journal of Electron Spectroscopy and Related Phenomena **110-111** (2000) 323-334.