

Study on changes of chemical structures at initial growth surface of carbon nanowalls

カーボンナノウォールの初期成長表面における化学構造の変化に関する研究

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Elemental composition, chemical bonding state and crystalline structure of initial growth surface of carbon nanowalls (CNWs) were investigated by Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). According to Raman spectra, it is found that nanodiamond structure exists in initially deposited thin carbon film. XPS analyses reveal that, when nanoislands grow on thin carbon film, chemical bonding state of C 1s changed from sp³ bonding to sp² bonding, and composition rate of fluorine drastically increased. These results indicate that nucleation of nanographene occurs in previously-deposited thin carbon film before its morphological change.

1. Introduction

Vertically-grown graphene sheets, so-called carbon nanowalls (CNWs), have attracted much attention as novel nanomaterials realizing new functional devices in recent years.^[2] It is due to the fact that the CNWs could possess several unique characteristics, such as ultrahigh aspect ratio, large surface-to-volume ratio, high carrier mobility and so forth. To control morphology of CNWs, it is important to clarify initial growth process of CNW, especially nucleation of nanographene. We have found that initial growth process of CNWs has 4 steps. According to scanning microscopy (SEM), the steps are as follows: (1) Deposition of thin carbon film, (2) Formation of nanoislands on the thin carbon film, (3) Nucleation of nanographene on the nanoislands, and (4) Vertical growth of CNWs. However, details of nucleation processes of nanographene have not clarified yet.

In this study, elemental compositions, chemical bonding states and crystal structures of initial growth surfaces of CNWs were investigated by Raman spectroscopy and X-ray photoelectron spectroscopy (XPS).

2. Experimental

CNWs were formed on Si substrates at a substrate temperature of 680°C using a multi-beam chemical vapor deposition system, which has two radical sources and an ion source consisting of radio frequency (13.56 MHz) inductively-coupled plasma sources.^[3] Flow rates of Ar, C₂F₆ and H₂ gases were 5, 10, and 6 sccm, respectively. The total gas pressure was set at 2.5 Pa. RF powers applied to Ar⁺

ion, CF_x and H radical sources were 200 W. An acceleration voltage of Ar⁺ ion was 100 V. Growth times were varied ranging from 2 to 50 min. Then, these samples were investigated by XPS and Raman spectroscopy.

3. Results and discussion

Fig.1 shows SEM images of initial growth surfaces of CNWs. With increasing growth times from 2 to 50 min, deposition of thin carbon film (2min), formation of nanoislands (5 min), nucleation (15 min) and growth of nanographenes (22 min and 50 min) were found in the SEM images. At that time, thicknesses of those samples increase from 0.8 to 35 nm.

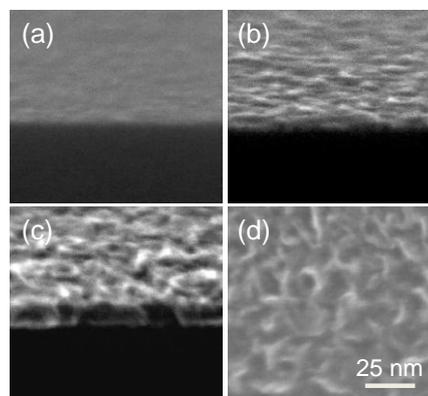


Fig.1 SEM images of initial growth surfaces of CNW: birds-eye view images at (a) 2min (b) 5 min and (c) 22 min, and (d) top-view image at 22 min.

Figure 2 shows Raman spectra of initial layer of

CNWs at growth time of 2 to 50 min. G-band (1600 cm^{-1}) and D-band (1350 cm^{-1}) were observed at all samples. The peak at 1450 cm^{-1} and 1550 cm^{-1} are derived from C-Si and O-O bonding states, respectively. At only 2 min, there is peak at 1320 cm^{-1} , which indicates existence of nanodiamond. Between 5 and 22 min, shapes of spectra hardly changed, however, the position of G-band peak slightly shifted to lower wavelength. In general, such the slight shift of G-band peak indicates increase of size of nanographene. From these results, at the initial growth stage of CNWs, thin carbon film which contains nanodiamond was firstly deposited, then nanoislands which consist of nanographene were formed. Size of nanographene hardly changes in the nanoislands. It starts to increase with its vertical growth.

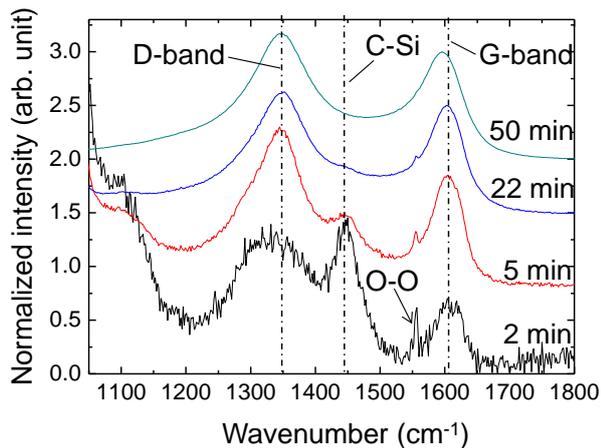


Fig.2 Raman spectra of initial layer of CNWs

Figure 3 shows C 1s spectra of initial layer of CNWs at growth time from 2 to 22 min. It is found that, between 2 min and 5 min, shapes of C 1s spectra drastically change and sp²-bond peaks (284.4 eV) become dominant. On the other hands, after 5 min, the peak position didn't change. This result indicates that the nucleation of nanographene occurs at the growth times from 2 min (thin carbon film) to 5 min (nanoislands). It is consistent with the result of Raman spectroscopy.

Figure 4 shows peak intensity ratio of F 1s/C 1s as a function of growth time. Between 3 min and 5 min, composition rate of F drastically increased. On the other hands, it didn't change after 5 min. This behavior corresponds with the change of C 1s spectrum. Therefore, it is deduced that change in fluorine content has some relation with nucleation of nanographene.

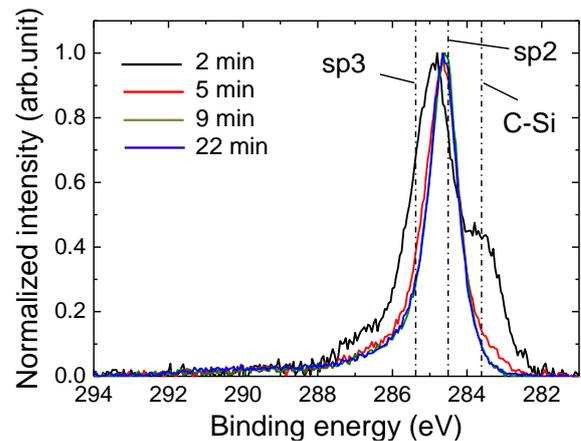


Fig.3 C 1s spectra of initial layer of CNWs at growth time of 2 to 22 min.

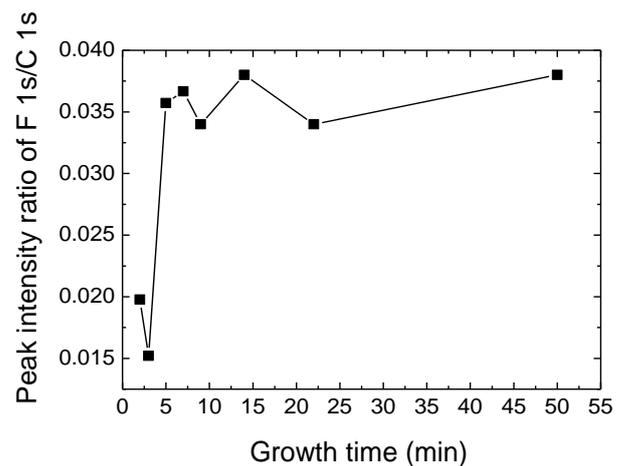


Fig.4 Peak intensity ratio of F 1s/C 1s as a function of growth time.

4. Conclusions

Elemental compositions, chemical bonding state and crystal structure of initial growth surface of CNWs were investigated. In this study, it was found that thin carbon film contains nanodiamond components, and size of nanographene increased with its vertical growth. On the other hand, XPS analysis showed that, when nanoislands were formed on the carbon film, chemical bonding state of carbon was changed from sp³ bonding to sp² bonding and composition rate of fluorine drastically increased. These results indicate that, at the nucleation of nanographene, change of bonding states occurs previous to morphological change.

References

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