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Soft X-ray absorption spectroscopy study of chemical states, orientation, and oxygen content of ion-irradiated vertically aligned multiwalled carbon nanotubes

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ABSTRACT

Low-energy Ar ions (0.5–2 keV) were irradiated onto vertically aligned multiwalled carbon nanotube (VA-MWCNT) films, and the chemical states, orientation, and oxygen content of the irradiated VA-MWCNT films were investigated by soft X-ray absorption spectroscopy (XAS). After irradiation, two additional peaks appeared in the XAS spectra in the C K region, indicating a significant change in the electronic structure. Furthermore, it was found that the VA-MWCNT films were oxidized after irradiation. The results of chemical-state analyses of the XAS spectra in both the C K and O K regions indicated the formation of carboxyl groups (—COOH) on the surface of the VA-MWCNT films upon irradiation. The oxygen content of the VA-MWCNT films increased with increasing ion energy and fluence.

1. Introduction

Nanostructured carbon materials such as carbon nanotubes (CNTs) [1] and graphenes [2] have been extensively studied toward the realization of potential nanodevice applications because of their intriguing properties. The morphology of the CNTs strongly determines the nanodevice applications. For example, vertically aligned multiwalled CNT (VA-MWCNT) films have been demonstrated to be applicable to nanodevices such as electron field emitters [3–5], sensors [6,7], supercapacitor electrodes [8], heat sink materials [9], and large-scale integrated (LSI) interconnects [10]. On the other hand, the irradiation of nanostructured carbon materials with energetic particles is considered to modify their structure and properties, and is applied to nanodevice fabrication [11,12]. It has been reported that spatially localized Ar ion irradiation of individual MWCNTs deposited on SiO_2 substrates can be used for the fabrication of quantum dots [13], and that Ar ion irradiation of MWCNTs enhanced the field-emission properties owing to defects introduced by the ion irradiation [14]. Moreover, the metal-semiconductor transition in CNTs upon electron irradiation of the CNTs has been demonstrated [15]. Several analytical techniques can be used to characterize irradiated nanostructured carbon materials. For example, Raman spectroscopy [16–18], transmission electron microscopy (TEM) [14,16,19], scanning tunneling microscopy (STM) [20], and X-ray photoelectron spectroscopy (XPS) [18,19,21] have been employed to study the properties and structures of irradiated nanostructured carbon materials. Among them, Raman spectroscopy is one of the most widely used tools. X-ray absorption spectroscopy (XAS) using synchrotron radiation (SR), on the other hand, is a powerful tool since it provides information on not only the local electronic structure surrounding excited carbon atoms, but also the orientation of the carbon π bonds [22]. However, only a limited number of XAS studies on CNTs, into which defects have been induced, have been reported [23]. In this study, to clarify the damage process of the MWCNTs and the chemical reaction upon irradiation, we irradiated VA-MWCNTs with low-energy Ar ions (0.5–2 keV) and investigated the chemical states, orientation, and oxygen content of the irradiated VA-MWCNT films by XAS.

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Table 1
Sample conditions.

Sample Number	Ar^+ Energy (keV)	Ar^+ Fluence (cm^{-2})
#1	as-prepared	
#2	0.5	5×10^{15}
#3	1	5×10^{15}
#4	2	5×10^{15}
#5	1	1×10^{16}
#6	1	5×10^{16}
#7	1	1×10^{17}

2. Experimental

VA-MWCNT films were grown on SiO_2 (200 nm)/Si substrate by catalytic thermal chemical vapor deposition. The average length and diameter of the MWCNTs were 160 μm and 23 nm, respectively. The TEM observation revealed the formation of MWCNTs with a hollow and multishell structure. Moreover, in the selected-area electron-diffraction pattern of the MWCNTs, the (002) and (004) planes of the graphite were clearly observed, which indicated the good crystallinity of the MWCNTs. We employed a Kaufman ion source (ULVAC-PHI, USG-3) to irradiate the VA-MWCNT films at room temperature with Ar ions. The incident energy ranged from 0.5 to 2 keV and the fluence varied between 5×10^{15} and 1×10^{17} cm^{-2}. Table 1 shows the sample conditions in this study. Seven samples (denoted by #1–#7) were prepared in the VA-MWCNT films under different irradiation conditions.

XAS measurements using a total electron yield (TEY) method were performed in the beamline BL-6.3.2 [24] at the Advanced Light Source (ALS). The photocurrent (I) of the sample induced by SR irradiation was monitored during SR photon energy scanning. The photocurrent of a gold plate (I_0) was also monitored as the incident SR beam intensity. Thus, the I/I_0 ratio provides the TEY. Scanning was performed in photon energy ranges of 270–310 eV (C K region) and 520–560 eV (O K region) in 0.1 eV steps. The estimated energy resolution ($E/\Delta E$) of the monochromatized SR beam was approximately 5000 with a 1200 lines/mm variable-line-spacing grating and a 40 μm exit slit. To evaluate the chemical states by a *fingerprint* method [25] and the O/C atomic ratios of the VA-MWCNT films, the X-ray absorption near-edge structure in the C K and O K regions of commercially available aromatic compounds having various oxygenated functional groups, namely, phloroglucinol (denoted by A1), 1,1′-bi-2-naphthol (A2), 1,4-dihydroxy-2-naphthoic acid (A3), 2,6-naphthalenedicarboxylic acid (A4), 9-anthracenecarboxylic acid (A5), mellitic acid (A6), syringic acid (A7), bianthrone (A8), anthraquinone-2-carboxylic acid (A9), and pyromellitic dianhydride (A10), was also measured. To evaluate the orientation of the VA-MWCNT films, the incident angle (α) of the SR beam to the sample plane was set to 15°, 30°,45°, 55° (magic angle), 75°, and 90° (normal incidence).

3. Results and discussion

From the TEY-XAS spectra in the 200–600 eV region of the VA-MWCNT films as-prepared and irradiated with Ar ions with highly oriented pyrolytic graphite (HOPG) as a reference, it was found that the profile of the as-prepared VA-MWCNT films was similar to that of HOPG. On the other hand, that of the irradiated VA-MWCNT films was different from that of the as-prepared VA-MWCNT films, and additional peaks were found in the O K region. Moreover, no peak in the Ar $L_{2,3}$ region was observed at around 250 eV, indicating that no Ar atoms existed on the surface of the VA-MWCNT films.

Fig. 1 shows the C K TEY-XAS spectra of the VA-MWCNT films as-prepared and irradiated by ions of different energies and fluences, with HOPG as a reference. The TEY intensity was normalized using

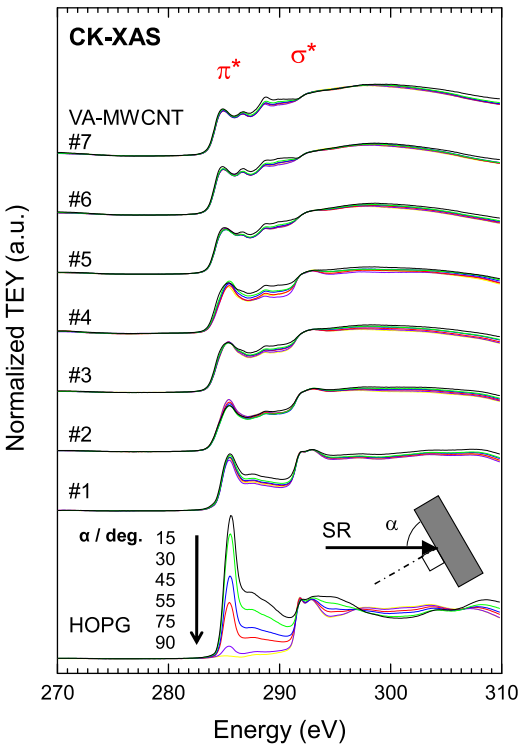

Fig. 1. C K TEY-XAS spectra of the VA-MWCNT films as-prepared and irradiated by Ar ions (energy: 0.5–2 keV, fluence: 5×10^{15}–1×10^{17} cm^{-2}), with HOPG as a reference. The spectra were measured at different α values.

the σ^* peak height at 292 eV. The spectra were measured at different α values. It is apparent that HOPG shows an inverse dependence of the π^* peak height at 285 eV with increasing α. On the other hand, for the MWCNT films as-prepared and irradiated, there is no α dependence of the π^* peak height.

The C K TEY-XAS spectra of the VA-MWCNT films as-prepared and irradiated by ions of different energies and fluences were taken at the magic angle with HOPG and carbon black (CB, N330) as references. An additional shoulder at ~289 eV was recognized after the irradiation. With increasing fluence, an additional peak at ~287 eV was recognized in the XAS spectra. Moreover, the spectra exhibit broad π^* peak profiles after the irradiation. CB generally exhibits a broad π^* peak profile [26]. This indicated that since the structure of CB exhibits an amorphous nature, the sp^2-hybridized carbon (sp^2-C) hexagonal ring network in the MWCNT films was destroyed and the film was amorphized. To analyze additional peaks after the irradiation, the C K region of the irradiated VA-MWCNT films was compared with reference compounds having various oxygenated functional groups. Fig. 2 shows the typical C K TEY-XAS spectra of the irradiated VA-MWCNT film #7 and 10 standard samples, which are aromatic compounds with various oxygenated functional groups (denoted by A1–A10). The spectra were taken at the magic angle. The spectra of the reference compounds showed a spectral fine structure characteristic of an oxygenated functional group. Consequently, the chemical states of oxygen can be analyzed by the *fingerprint* method using the spectral fine structures. From the comparison between the spectral features of the π^* peak in the C K region for the irradiated MWCNT film #7 and the standard samples, the peak at ~289 eV was found to nearly correspond to the peaks of A3–A7 originating from carboxyl groups (—COOH). On the other hand, the peak at ~287 eV may be a characteristic of the carbonyl groups (>C=O) observed in A8 and A9.

Fig. 3 shows the O K TEY-XAS spectra of the VA-MWCNT films as-prepared and irradiated by ions of different energies and fluences.

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