



Formation of carbon-nanostructure from X-ray induced defect in single-walled carbon nanotubes



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ABSTRACT

We have studied annealing effects on X-ray irradiated single-walled carbon nanotubes (SWNTs) by confocal micro-Raman scattering spectroscopy. The SWNT films irradiated with 1254-eV X-ray were annealed in argon atmosphere with increasing the temperature from 200 °C to 500 °C by 100 °C. We found that a new Raman peak at $\sim 1130\text{ cm}^{-1}$ came into existence after the annealing at 300–400 °C. The 1130-cm^{-1} peak was grown by the annealing exclusively in the X-ray irradiated sample. It is presumable that the 1130-cm^{-1} peak is ascribed to carbon nanostructure formed by the annealing of the X-ray irradiated SWNT. Based on the comparison of spatial images of Raman intensity, the nanostructure responsible to the 1130-cm^{-1} peak is likely formed by aggregation of interstitial carbon atoms diffused on SWNT surface. Because of the comparison of the probe wavelength dependence of the peak frequency with previous reports, we concluded that polyacetylene-like structures are formed by the post-irradiation annealing of SWNT.

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1. Introduction

Irradiation of carbon nanotubes (CNTs) by electrons, [1–3] ions, [4,5] and X-ray [6–9] forms defects in hexagonal carbon lattice. The defects in materials are generally considered to be obstacles for intrinsic properties. However, in nano-sized materials like CNTs, structural change induced by defect formation may give rise to modification of their electrical properties. Hence, clarification of detailed properties of the defects is essential subject for controlling the characteristic features and quality of nano-sized materials. Urita et al. [1] demonstrated that the electron irradiation formed Frenkel defects, vacancy-interstitial pairs, in double-walled CNTs (DWNTs). Their experimental results showed that defect concentration is governed by the competition between formation and annihilation reactions and strongly depends on a sample temperature during the irradiation. The interstitial carbon atom diffuses with ease on CNTs surface. [7] Hence, when the X-ray-induced defects formed at high concentration, the thermal annealing of the irradiated CNTs may give rise to not only modification of tubes but also aggregation of interstitial atoms.

In the present paper, we have reported the results of Raman scattering study on the single-walled CNTs (SWNTs) annealed after X-ray irradiation. When the X-ray induced defects were annealed at 300–400 °C in inert gas atmosphere, we found a new Raman peak formed at $\sim 1130\text{ cm}^{-1}$. Because of the comparison of the probe wavelength dependence of the peak frequency with previous reports, we concluded

that the peak is attributed to nanostructures formed by the post-irradiation annealing of the X-ray irradiated SWNTs. We suggested that the peak is related to polyacetylene-like structures formed via thermal diffusion and aggregation of interstitial atoms.

2. Experiment

SWNT powder synthesized by CoMoCAT-CVD method was purchased from Aldrich Co., Ltd. The mean diameter of the SWNTs was $\sim 0.9\text{ nm}$, evaluated by Raman measurements. The sample powder was dispersed in the aqueous solution of 1.0-wt% sodium dodecyl sulfate (SDS) using a horn-type ultrasonic homogenizer and centrifuged at 21,500 g for 10 min in order to remove the catalyst particles and carbon impurities. The unsolved supernatant was filtered using a mixed cellulose ester membrane. The SWNT films were transferred on silicon substrates by removing the membrane with acetone vapor in a sealed container. The SWNT samples were attached on the sample stage in the evacuated chamber at the base pressure 10^{-5} Pa and irradiated with the X-ray of 1254 eV for 2 h in vacuum in order to form Frenkel defects in SWNTs. [8,9] The irradiated sample was isochronally annealed at from 200 to 500 °C in Ar atmosphere for 30 min. In the annealing procedure, the temperature was raised by 100 °C.

The pristine, irradiated, and annealed samples were characterized by Raman scattering spectroscopy at room temperature. Raman spectra with a broad range were measured using a conventional Raman system (JASCO NRS-3100) with 532-nm laser beam as the probe. The spatial distributions of Raman intensity (Raman images) were measured using a confocal Raman system equipped with a piezo-drive stage

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(WITec alpha300SRA+) with 532-nm and 633-nm probe beam. For multiwavelength Raman scattering spectroscopy, we used a system comprising a double monochromator (SPEX 1404), a liquid-nitrogen-cooled CCD detector (Roper PyLon100BR), and five probe lasers: 457 (2.71), 515 (2.41), 532 (2.33), 561 (2.21), and 660 nm (1.88 eV).

3. Results

Fig. 1 shows typical Raman spectra of the pristine, irradiated, and post-irradiation annealed (200–500 °C) samples. We clearly observed G band (tangential vibration mode), and D band (defect induced mode) in the spectra. An inset in the Fig. 1 shows RBMs (radial breathing modes) of pristine sample. According to the dependence of the RBM frequency (Ω_{RBM}) on the SWNT diameter (d), $d = 248/\Omega_{RBM}$ [10], the strongest peak observed at ~ 270 cm^{-1} can be ascribed to the SWNT with a diameter of ~ 0.9 nm. Thus, the sample used in the present study mainly comprised the SWNT with a diameter of 0.9 nm. The X-ray irradiation enhanced the D band strongly without large change of the G band. The result shows that the irradiation gave modest changes in SWNT structure, suggesting that the irradiation-induced defects are almost isolated. The annealing after the irradiation in Ar atmosphere, post-irradiation annealing, reduced defects as shown by the decrease of the D band intensity. The detail of the defect recovery process was discussed in Ref. 8. Besides these reported changes, we found that a new peak came into existence at ~ 1130 cm^{-1} (marked by arrows in Fig. 1) by the annealing at 400 °C. The peak was annealed out at 500 °C.

In order to examine whether the 1130- cm^{-1} peak is relevant to the X-ray irradiation effect, we carried out similar annealing experiments for both unirradiated and thermally oxidized samples. The defects in the thermally oxidized sample are dominantly vacancies because the oxidized carbon atoms are emitted by the form of carbon dioxide or carbon monoxide. We found no growth of 1130- cm^{-1} peak in these samples after the annealing at 400 °C in Ar (figure was not shown). Consequently, the 1130- cm^{-1} peak is relevant to carbon nanostructures grown in the

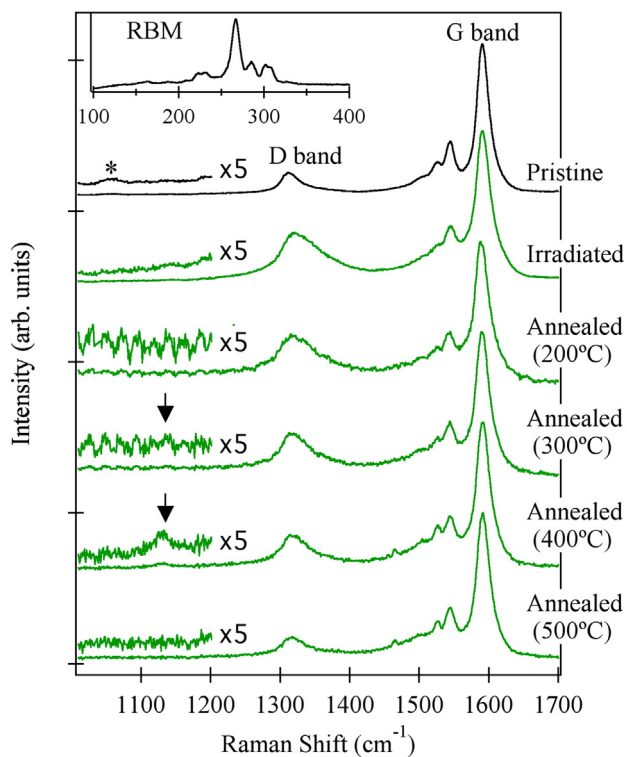


Fig. 1. Raman spectra of pristine, X-ray-irradiated, and annealed SWNTs. The inset is RBMs of pristine SWNTs. The five times signals of each spectrum between 1000 and 1200 cm^{-1} are displayed.

post-irradiation annealed samples but not to small amount of impurities, such as the catalyst particles or the amorphous carbons in the samples.

We calculated the images of the following Raman intensity ratios: 1130- cm^{-1} peak/G and D/G of the sample annealed at 400 °C. The results are shown in Fig. 2, together with the image of the G-band intensity of the same sample. In the images, we obtained larger intensity ratio in the brighter spot. The image of D/G of Fig. 2 (a) shows the distribution of the center responsible to the D band, while the image of the G-band intensity of Fig. 2 (c) shows the spatial distribution of SWNTs in the sample. The spatial distribution of the bright and dark regions in the image of 1130- cm^{-1} peak/G is rather similar to that of the D/G image. It is suggested that the structure responsible to the 1130- cm^{-1} peak is formed near the SWNTs affected by the X-ray irradiation.

We show the Raman spectra around the 1130 cm^{-1} measured with five probe energies in Fig. 3 (a). It is evident that the peak shifted to higher side with higher probe energy. The peak position ($\Omega_{1130\text{-peak}}$) is proportional to the probe energy (E_{prob}) as shown in Fig. 3 (b), and the relation is approximated by $\Omega_{1130\text{-peak}} = 26E_{\text{prob}} + 1073$.

4. Discussion

In order to clarify the origin of the 1130- cm^{-1} peak, we compared our results with the similar Raman peaks previously reported by other groups. Fantini et al. [11] measured Raman spectra of as-grown SWNT samples and observed a peak at ~ 1050 cm^{-1} . They ascribed the peak to C–O–C vibration due to the impurities adsorbed on the SWNT. They showed that the peak position does not rely on the Raman probe energy, which is not consistent with our results. The C–O–C vibration that reported by them was observed in the pristine SWNT samples in the present study (marked by an asterisk in Fig. 1). The peak was however vanished by the X-ray irradiation, indicating that the X-ray irradiation cleaned the SWNT surface up.

Herziger et al. [12] studied Raman spectra of ion-irradiated graphenes. Besides large enhancement of defect-induced mode (D band) by the irradiation, D/G > 1, they found another defect-induced Raman peak around 1100 cm^{-1} . They called this peak as D'' band. They reported the peak frequency of the D'' band depended on the Raman probe energy; the peak shifted to the lower frequency side with higher probe energies. This probe-energy dependence is opposite from that of the 1130- cm^{-1} peak found in the present study. Moreover, there is large difference in the defect density between their study and the present study.

The peak at ~ 1150 cm^{-1} in the Raman spectra of poor quality CVD-diamond was analyzed by several groups. [13–15] Ferrari et al. [15] studied the Raman spectrum of CVD-diamonds in detail and suggested that the 1150- cm^{-1} peak should be relevant to polyacetylene formed as a precursor of the CVD-diamond. They demonstrated that the peak frequency shifted to higher frequency side with higher probe energy. This probe-energy dependence is in good agreement with our results. Therefore, we concluded the new Raman peak at ~ 1130 cm^{-1} , we firstly found, was ascribed to polyacetylene-like structures on SWNTs.

Let us discuss the growth mechanism of the polyacetylene-like structures in the X-ray irradiated SWNTs by thermal annealing. We present two additional experimental results as follows. First, we observed no growth of 1130- cm^{-1} peak in the X-ray irradiated large-diameter SWNTs ($d \sim 1.4$ nm) by thermal annealing at 400 °C. The result is consistent with our previous report that thermal stability of defects of large-diameter SWNTs is lower than that of small-diameter SWNTs. [8] It is presumable that the interstitial carbon atoms in large-diameter SWNTs recombine with vacancies more easily than those in small-diameter SWNTs. Secondly, when we used an annealing system which had much residual air or air leakage to anneal the X-ray-induced defects on SWNTs, the 1130- cm^{-1} peak was not found in the post-irradiation annealed sample. We speculated that the diffused interstitial carbon atoms or the polyacetylene-like structures are immediately burned in

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