

Threshold Energy of Low-Energy Irradiation Damage in Single-Walled Carbon Nanotubes

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Low-energy electron and photon irradiation cause damage in single-walled carbon nanotubes. In this work, irradiation effects of photons ($h\nu < 20$ eV) in an ultra-high vacuum were systematically studied. The threshold energy of the low-energy irradiation damage was evaluated to be about 6 eV. Less damage was observed at 8 eV, which seems to be due to a small optical absorption coefficient at that energy. [DOI: 10.1143/JJAP.47.2040]

KEYWORDS: Raman scattering, G-band, D-band, radial breathing mode, defect formation barrier

1. Introduction

Single-walled carbon nanotubes (SWNTs) are damaged by electron or photon irradiation¹⁾ even when the energy of incident particles is much lower than the threshold energy of knock-on damage (~ 86 keV for an electron²⁾ and γ -ray region for a photon). The low-energy irradiation damage extinguishes the Raman and photoluminescence spectra, reduces the chemical tolerance, and converts the electric properties of a metallic SWNT to semiconducting.¹⁾ The irradiation-induced defects have some characteristic properties.¹⁾ That is, the formation and healing of the defects is reversible, indicating that the number of carbon atoms is preserved. The activation barrier for the defect healing depends on the diameter of the SWNT (larger barrier for smaller diameter). The defects are healed even at room temperature or below, for a typical SWNT (diameter of ~ 1 nm).

Evaluating the defect formation and healing barrier would be important for clarifying the defect structure and the defect formation mechanism. In our previous report, the activation barrier for the defect healing was estimated to be ~ 1 eV, depending on the diameter.³⁾ On the other hand, the defect formation barrier is not clear, except that we know it is less than 20 eV.⁴⁾ Determining the defect formation barrier is also practically important because low-energy electrons, photons, or ions are often used as analytical and lithographic tools.

In this work, irradiation effects of photons, whose energy is less than 20 eV, were studied to determine the threshold energy of the low-energy irradiation damage in SWNTs.

2. Experimental Procedure

SWNTs were grown on a SiO₂/Si substrate by the thermal chemical vapor deposition method using ethanol as a carbon source and Co as catalyst. The growth temperature was 850 °C.

Photon irradiation was performed at the beamline BL1B in the ultra-violet synchrotron orbital radiation (UVSOR) facility of the Institute for Molecular Science, Okazaki. The synchrotron radiation light was monochromatized by a Seya–Namioka monochromator. The irradiation dose was $\sim 5 \times 10^{17}$ cm⁻², unless otherwise mentioned. The irradiation was performed at room temperature in an ultra-high vacuum of less than 5×10^{-7} Pa.

The irradiation damage was evaluated by resonance Raman measurements, with the excitation wavelength of

785 nm. The measurements were performed in air at room temperature.

3. Results

Wide-range Raman spectra of pristine and irradiated SWNTs are shown in Fig. 1. In this study, we prepared samples for each photon energy. However, some differences were observed, especially in the spectral intensity and G/radial breathing mode (RBM) intensity ratio. We thus show spectra of pristine and irradiated SWNTs for each photon energy. The spectra of different samples (photon energies) were normalized by the G-band intensity of the pristine samples. The spectra of pristine and irradiated SWNTs were normalized by the Si peak intensity at 520 cm⁻¹.

The irradiation dose of the 0th-order (unmonochromatized) light is at least a few orders of magnitude larger than in other cases (5×10^{17} cm⁻²). The irradiation was performed through a pyrex window to cut high-energy photons. The window is almost transparent and opaque for $h\nu \leq 3.5$ eV, and $h\nu \geq 4.5$ eV, and the transmittance is about 50% at $h\nu = 4$ eV. The irradiation of 3 eV was also done through the window to cut higher-order light. The irradiation of 4 eV or higher energies were performed without the window. The irradiation dose for 16 eV was about half of that in other cases, due to beam-time limitation.

Figure 2 shows G- and D-band spectra of pristine SWNTs and SWNTs irradiated by 0th-order light and 4 to 7 eV photons. No spectral change was observed by the 0th-order light irradiation, although the irradiation dose is extremely large in this case. This indicates that, at least in an ultra-high vacuum, SWNTs are not damaged by irradiation of photons whose energy is less than ~ 4 eV. Almost no spectral change was observed after monochromatized light irradiation of 4 and 5 eV, either. A clear indication of the damage, a D-band intensity increase, was first observed at 6 eV. At 7 eV, the D-band intensity increase is also obvious. The photon energy dependence of the D-band intensity increase and G/D ratio decrease caused by the irradiation are summarized in Figs. 3 and 4, respectively. At 5 eV or below, the irradiation hardly changed the spectra. On the other hand, at 6 eV and above, an apparent increase of the D-band intensity and decrease of the G/D ratio were observed. These results mean that the threshold energy of low-energy irradiation damage is located between 5 and 6 eV.

The damage also decreases the G-band and RBM intensities.¹⁾ Figures 5(a) and 5(b) show the G-band and

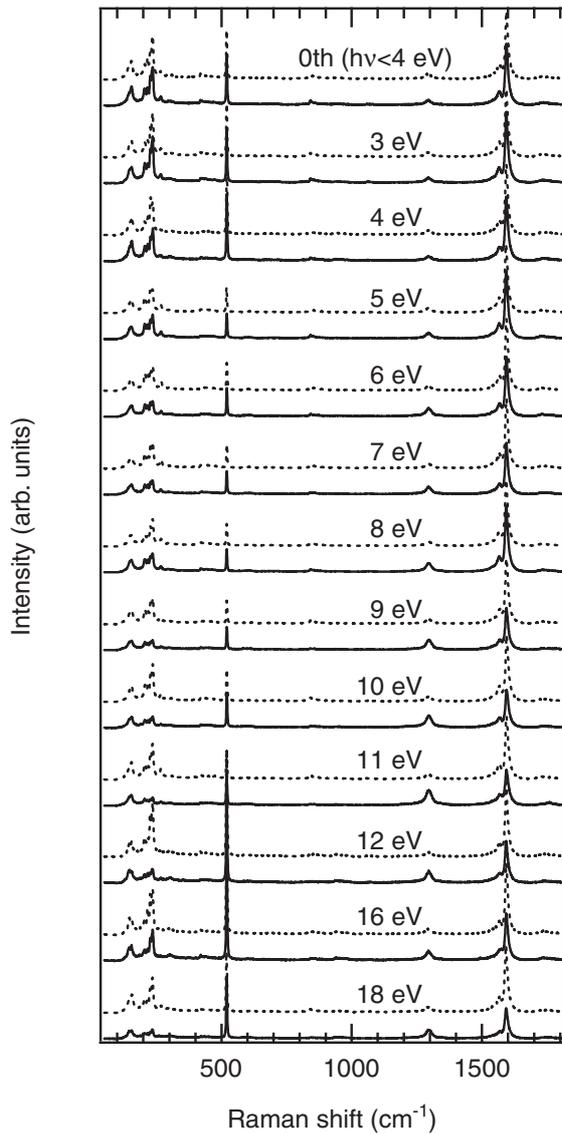


Fig. 1. Wide-range Raman spectra of pristine SWNTs (dotted line) and SWNTs irradiated by the 0th-order and 3–18 eV light (solid line). The irradiation dose was $\sim 5 \times 10^{17} \text{ cm}^{-2}$ except for the 0th-order light (very large dose) and for 16-eV (half dose).

RBM spectra of pristine and irradiated SWNTs. At $h\nu \geq 6 \text{ eV}$, the decreases were apparently observed (except for $h\nu = 8 \text{ eV}$, see below). The intensity decrease is not accompanied by spectral broadening. Considering that the Raman spectra from SWNTs are detectable owing to the resonance enhancement effect, the intensity decrease seems to be caused by a reduction of the resonance effect, which is probably due to damage-induced broadening of absorption spectrum. The intensity of minor peaks observed at ~ 840 and 1740 cm^{-1} , which have been assigned to an out-of-plane transverse optical phonon mode and its overtone,⁵⁾ were also decreased by the damage, as seen in Fig. 1. The D-band intensity also finally takes a downward turn when the damage becomes severe, as shown in our previous report.⁶⁾ In Fig. 5(b), the diameter dependence of the damage⁴⁾ is clearly observed again.

The G-band and RBM intensity decreases are summarized in Fig. 5(c). The results show that, at $h\nu = 8 \text{ eV}$, the intensity decreases are less prominent, although the occur-

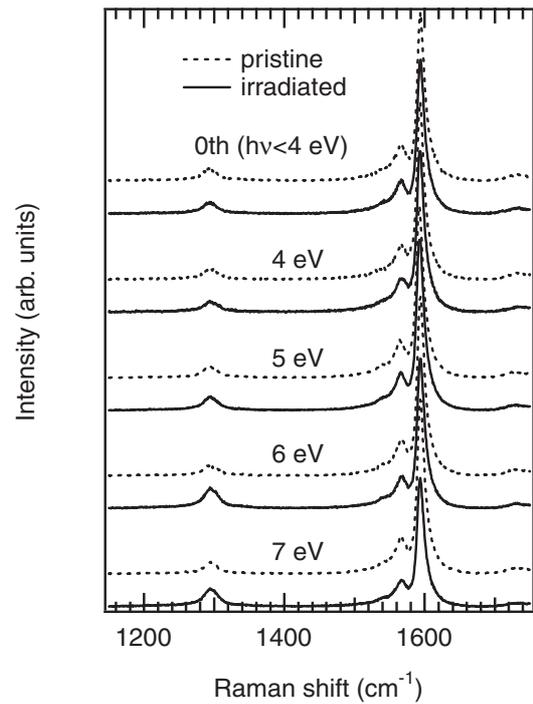


Fig. 2. G- and D-band spectra of pristine SWNTs and SWNTs irradiated by the 0th-order and 4–7 eV light.

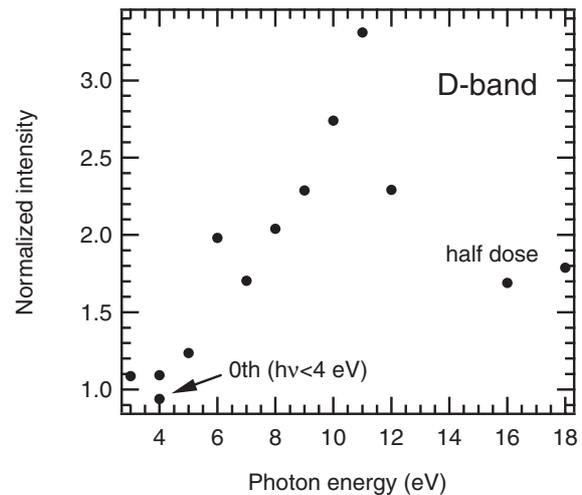


Fig. 3. Normalized D-band intensity after the irradiation.

rence of the damage at the photon energy is apparent from the increase of the D-band intensity (Fig. 3) and decrease of the G/D ratio (Fig. 4). This means that the G-band and RBM intensities are less sensitive to the D-band intensity at a small defect density and that the SWNTs are less damaged at $h\nu = 8 \text{ eV}$. We think that the less damage at 8 eV is due to a small absorption coefficient. The optical absorption coefficient $\alpha(\omega)$ is closely related to the imaginary part of the dielectric function $\epsilon_2(\omega)$, as $\alpha(\omega) = 2\pi\epsilon_2(\omega)/\lambda n(\omega)$, where, λ is wavelength and n is the refractive index. The $\epsilon_2(\omega)$ of SWNTs in a wide energy range has been studied by a means of transmission electron energy loss spectroscopy (EELS). According to previous EELS studies,^{7,8)} $\epsilon_2(\omega)$ of SWNTs considerably varies (factor of ~ 5) in a photon energy range

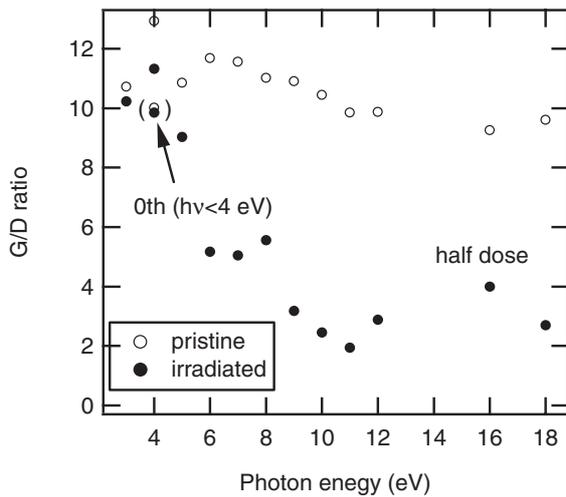


Fig. 4. G/D area ratios of pristine and irradiated SWNTs.

of 3–18 eV. It has a local minimum at about 8 eV, meaning that the absorption coefficient is small at that energy. On the other hand, $\epsilon_2(\omega)$ has been reported to have a local maximum at ~ 11.5 eV, and to monotonically decrease at higher energies. This is also consistent with the severe damage observed near that energy [Figs. 3, 4, and 5(c)]. The relation between the severity of the damage and absorption coefficient strongly suggests that the defect formation follows the electronic excitation in SWNTs.

4. Discussion

A schematic energy diagram of the defect formation and healing suggested by our present and previous studies is shown in Fig. 6. From our previous results, the healing barrier was estimated to be about 1 eV, depending on the diameter.³⁾ Owing to the small barrier, the defect can be healed even at room temperature. The nominal healing barrier would become larger due to chemisorption to defect sites. Multiple defect formation would also increase the healing barrier. The present results show that the formation

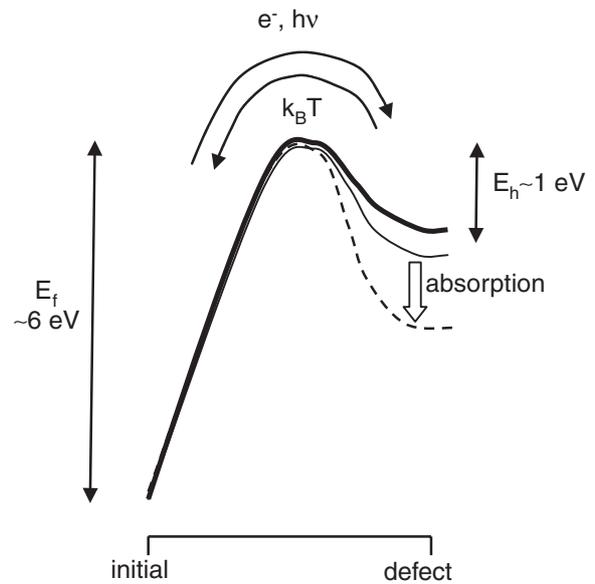


Fig. 6. Schematic energy diagram of the formation and healing of the low-energy irradiation-induced defect. E_f and E_h are formation and healing barriers. The thick and thin solid curves denote thick and thin SWNTs. The defect may be largely stabilized by gas absorption (dashed curve).

barrier is about 6 eV. Considering that the activation barrier for defect healing is ~ 1 eV, the defect formation energy is estimated to be about 5 eV. We do not exclude the possibility that the defect formation barrier also depends on the diameter. However, all RBM intensities of semi-conducting SWNTs observed at 205 (d : ~ 1.2 nm) to 235 cm^{-1} (1.0 nm) started to decrease at 6 eV, as shown in Fig. 5(b).

As discussed in our previous paper,³⁾ most of well-known and well studied defects, such as vacancy and Stone–Wales defects, do not seem to be consistent with the experimental results. Very recently, Okada proposed an adatom–vacancy model as a possible explanation for the low-energy irradi-

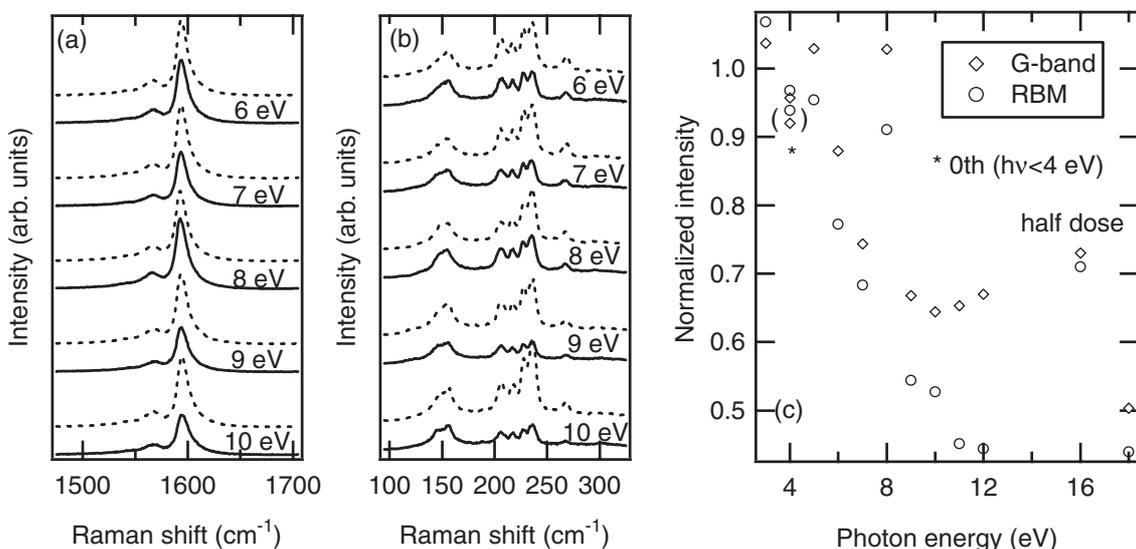


Fig. 5. G-band (a) and RBM (b) spectra of pristine SWNTs and SWNTs irradiated by 6–10-eV photons. (c) Normalized intensities of irradiated SWNTs.

ation-induced defects.⁹⁾ The defect is formed by breaking two of three bonds of a carbon atom in a SWNT. According to his calculation, the defect formation barrier is ~ 10 eV and slightly depends on the chirality and relative orientation of the defect and tube axis. There is still a quantitative difference between the experimental and calculation results. However, the calculation was performed for an isolated SWNT, whereas, in the present study, most of the SWNTs were likely to have formed bundles. The defect formation energy and barrier may be considerably reduced if another adjacent graphene layer exists and some chemical bonds between the two layers are formed via the defect. Further studies are needed to clarify the defect structure.

Regardless of the detailed defect structure, another very important and interesting issue is how the atomic displacement is caused by the low-energy electronic excitation. The momentum of a low-energy photon (even an electron) is not at all sufficient to directly move a carbon atom in a graphene network. Considering that the photon flux density used in this study was only $\sim 10^{14}$ cm⁻² s⁻¹, the defect seems to be simply caused by a single-photon process, not by a multi-photon process. To our knowledge, such low-energy irradiation damage has not been reported for graphite or for most metals and semiconductors, in which the electronic states are not localized. Some mechanism for localization of an excited electron (hole) might be necessary to explain the defect formation. A detailed understanding of excited electronic states may be crucial. We point out that low-energy stimulated bond breaking and displacement of an atom have also been observed at semiconductor surfaces¹⁰⁾ and at defects.¹¹⁾ A low-energy-induced structural change also is known to occur in bulk C₆₀.¹²⁾

5. Conclusions

SWNTs were irradiated by photons of $h\nu < 20$ eV in an ultra-high vacuum and the damage was evaluated by resonant Raman spectroscopy. The threshold energy of low-energy irradiation damage was determined to be about 6 eV. Less damage was observed at 8 eV. This is ascribed to a small optical absorption coefficient at that energy. Further studies are necessary to clarify the detailed defect structure and the mechanism of the defect formation.

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- 1) S. Suzuki and Y. Kobayashi: *Mater. Res. Soc. Symp. Proc.* **994** (2007) F04-02, and references therein.
- 2) B. W. Smith and D. E. Luzzi: *J. Appl. Phys.* **90** (2001) 3509.
- 3) S. Suzuki and Y. Kobayashi: *J. Phys. Chem. C* **111** (2007) 4524.
- 4) S. Suzuki and Y. Kobayashi: *Chem. Phys. Lett.* **430** (2006) 370.
- 5) V. W. Brar, Ge. G. Samsonidze, M. S. Dresselhaus, G. Dresselhaus, R. Saito, A. K. Swan, M. S. Unlu, B. B. Goldberg, A. G. Souza Filho, and A. Jorio: *Phys. Rev. B* **66** (2002) 155418.
- 6) S. Suzuki, D. Takagi, Y. Homma, and Y. Kobayashi: *Jpn. J. Appl. Phys.* **44** (2005) L133.
- 7) R. Kuzuo, M. Terauchi, M. Tanaka, and Y. Saito: *Jpn. J. Appl. Phys.* **33** (1994) L1316.
- 8) T. Pichler, M. Knupfer, M. S. Golden, and J. Fink: *Phys. Rev. Lett.* **80** (1998) 4729.
- 9) S. Okada: *Chem. Phys. Lett.* **447** (2007) 263.
- 10) J. Kanasaki, T. Ishida, K. Ishikawa, and K. Tanimura: *Phys. Rev. Lett.* **80** (1998) 4080.
- 11) A. Hida, Y. Mera, and K. Maeda: *Physica B* **308–310** (2001) 738.
- 12) J. Onoe, T. Nakayama, M. Aono, and T. Hara: *Appl. Phys. Lett.* **82** (2003) 595.