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Raman Scattering of Single-Walled Carbon Nanotubes Implanted with Ultra-Low-Energy Oxygen Ions

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Single-walled carbon nanotubes (SWNTs) implanted with ultra-low-energy oxygen (O⁺) ions have been studied by means of Raman scattering experiments. The relative intensities of the D-band related to some defects increase with the O⁺ dose in the Raman spectra of the implanted samples. Although no recognizable shift of phonon energies due to the ion implantation has been observed, the intensities of the Stokes and anti-Stokes lines originated from radial breathing modes of SWNTs which exhibit various behaviors due to degree of the implantation, indicating that the resonant energies are changed. To explain these findings, the structure and the electronic states of SWNTs with substitutional O impurities have been studied by applying theoretical calculations based on the first principle method and a tight-binding method. As a result, it has been suggested that the incorporation of oxygen atoms at carbon sites is plausible, and the experimental observation can thus be consistently explained on the basis of the O impurities in SWNTs.

KEYWORDS: carbon nanotube, oxygen ion implantation, ultra-low energy, Raman scattering, first principle pseudopotential method, tight-binding model

1. Introduction

Many studies on single-walled carbon nanotubes (SWNTs) with the goal of their practical application have been reported in the last decade.1,2) The SWNT structures can be considered to be graphene sheets rolled up at certain angles, and depending on the diameter and chirality, the electric character of SWNTs becomes metallic or semiconducting. Because of their unique electrical and optical properties due to their one-dimensionality, it has been expected that SWNTs will be useful in nanoscale devices: field-effect transistors (FETs) with SWNTs are particularly promising for highly sensitive biosensors3) and chemical sensors.4)

In general, semiconducting SWNTs grown by chemical vapor deposition (CVD) have p-type characteristics, and act as p-type channels in FETs.5) In order to fabricate various devices, the control of carrier type, as n or p, and carrier concentration in SWNTs is necessary. There have been several proposals for means of obtaining n-type SWNTs: annealing of SWNTs in vacuum, the introduction of Gd as a dopant,6) the deposition of alkali metals on SWNTs,7) and so on. The control of a Schottky barrier which may exist at the electrode-SWNT contact may also affect the carrier type of the SWNT channels in FETs.5) However, effective methods for controlling the carrier type have not been established yet.

In the previous work, we suggested that ultra-low-energy O⁺ implantation may be promising for controlling n-type carrier in SWNTs.8) The O⁺ beam energy is approximately 25 eV which is near to the exchange energy between O and C atoms in graphite, and therefore, the effective exchange of atoms without large damage is expected. The FETs with SWNT irradiated with ultra-low-energy O⁺ ions have shown a transition from p-type to n-type characteristics that corresponds to the O⁺ dose.5) On the basis of observations by means of the electron energy loss spectroscopy, it has been suggested that oxygen atoms can be doped into the interstitial and/or substitutional sites.5)

To clarify the electrical characteristics of SWNT implanted by ultra-low-energy O⁺ ions, Raman scattering experiments are carried out in the present study. The effects of the O⁺ irradiation on the electronic states are clarified by the resonant effects on the Stokes and anti-Stokes lines that reflect the radial breathing modes (RBMs) in SWNTs. To clarify them in further detail, the structure and the electronic states of SWNTs with O impurities have also been examined theoretically.

2. Experimental

By CVD with ethanol vapor as a carbon source, SWNTs were grown on (100) Si substrates with catalysts that were prepared by the following method. The methanol solution of Fe(NO₃)₃·9H₂O, MoO₂(acac)₂ and alumina nanoparticles was deposited on the substrate surfaces. These substrates were pre-heated up to 120°C for 3 min in air, and then set into a furnace with a 5-cm-diameter tube of SiO₂, to be heated at 900°C in an Ar atmosphere to bring them close to thermal equilibrium. At 900°C, an ethanol vapor was provided for 10 min to grow the SWNTs. During CVD growth, the pressure in the furnace was approximately 2 Torr. Dense SWNT bundles were grown so as to cover almost the entire substrate surfaces, as confirmed by means of observation through scanning electron microscopy. A very rough estimation suggests that the order of the C density was about 10¹⁵–10¹⁶ atoms/cm², suppose that the mono-layer of SWNTs was grown on the substrate. Finally, the samples were cooled to room temperature in an Ar atmosphere.

Implantation of O⁺ ions into the samples was carried out at the ultra-low ion energy of 25 eV in a vacuum of

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10^{-9} \text{ Torr. In the present study, three doped samples were prepared: their estimated doses of O^+ ions were 2.7 \times 10^{11}, 3.2 \times 10^{12} and 3.2 \times 10^{13} ions/cm^2. The average O/C ratio was roughly estimated to be in the order of 10^{-4} through 10^{-2} based on the use of the values of density and the dose of the implantation.}

In the Raman scattering experiments, 488.0 and 514.5 nm lines from an Ar ion laser were used as the excitation light, and were focused on the sample surface with a diameter of approximately 10 \mu m by a microscope objective lens. A charge-coupled-device camera cooled by liquid nitrogen was used for the detection of the Raman scattering light, which was dispersed through a triple grating monochromator with a filtering stage.

3. Results

Figure 1 shows the Raman spectra of the as-grown and O^+ implanted SWNTs excited by the 514.5 nm laser line in the high-frequency region from 1200 to 1700 cm^{-1}. Spectral intensities were normalized according to the peak of the G-band, at approximately 1350 cm^{-1}. In all spectra, the zone-holding side-band on the low-energy side of the G-band and the D-band at approximately 1350 cm^{-1} are recognizable. The intensity ratio of G-band to D-band decreases from 7.2 to 3.3 as the dose of O^+ irradiation increases from 0 to 3.2 \times 10^{13} ions/cm^2. This decrease of the G/D ratio implies an increase in the number of defects introduced to the SWNTs by the O^+ irradiation.

The Raman spectra of the samples excited by 514.5 nm light in the low-frequency region from 60 to 250 cm^{-1} are shown in Fig. 2. The right half of the figure shows the Stokes scattering spectra, while the left half shows the anti-Stokes scattering spectra. In both the Stokes and anti-Stokes spectra, several peaks due to RBMs in the SWNTs are clearly apparent. Since these spectra have not been normalized according to the Bose factor, the intensities of the lower frequency phonons are somewhat emphasized. On comparing the spectra of O^+ irradiated samples with that of an as-grown sample in detail, it is apparent that the peaks at approximately -171, -140, -119, 119, 140 and 171 cm^{-1} indicated by solid lines in the figure disappear under the irradiation, while the peaks at approximately -129 and 129 cm^{-1} indicated by dashed lines appear abruptly. Such marked changes exceed possible experimental ambiguity. Other peaks also exhibit some remarkable changes in their intensities due to the irradiation. However, no frequency change in the RBM due to the irradiation is observed within the experimental accuracy.

In the Raman scattering spectra under the excitation of a 488.0 nm laser line, similar behavior in the intensities of RBMs is also observed as shown in Fig. 3. Peaks that disappear due to the irradiation are located at approximately -180, -117, 117 and 142 cm^{-1} as indicated by the solid lines, while peaks appear at approximately -133 and 160 cm^{-1} as indicated by dashed lines. It should be noted that the behavior of some peaks differs between the Stokes and anti-Stokes spectra, for example, the peak at 160 cm^{-1}
in Fig. 3 is not observed in the Stokes spectra of as-grown sample but appears in those of the irradiated samples, whereas the corresponding peak at $-160 \text{ cm}^{-1}$ is observed in the anti-Stokes spectra of all samples.

The above described spectral changes cannot be explained by any inhomogeneity in samples since the spectra of the irradiated samples are similar to each other but appear to be different to that of the as-grown sample. Various dependences on the $O^+$ dose among the spectra of the three implanted samples are also observed.

4. Discussion

4.1 D-band intensities

Discussion should begin with a consideration of the G/D intensity ratio which clearly decreases from 7.2 to 3.3 as the $O^+$ dose increases, as shown in Fig. 1. This decrease of G/D implies an increase in the number of defects introduced to the SWNTs by the $O^+$ irradiation, since the origin of the D-band has been considered to be based on the double resonance effect in graphite. 2)

In a simple explanation of the Raman scattering process, first, an electron is excited to a state with momentum $k$ and energy $E_k$. Then the excited electron is scattered by absorbing or emitting a phonon with momentum $q$ and energy $\omega$: that is, $k \rightarrow k + q$, $E_k \rightarrow E_k \pm \omega$. Finally, the electron emits the photon with energy $E_k \pm \omega$ in transition to the ground state. In the conventional Raman process the momentum $k \pm q$ of the electron which emits the photon should be equal to the momentum $k$ of electrons excited by the incident light, because of the total momentum conservation rule in the process. Therefore, in the electron-phonon scattering $k \rightarrow k + q$, only LO phonons which have the momentum $q = 0$ are responsible for Raman scattering. Regarding the energy in the process, Raman scattering is significantly enhanced when one of the electron energies $E_k$ and $E_k \pm \omega$ coincides with one of the incident and emitted photon energies. This resonance effect occurs in the Raman spectra of SWNTs in the present experiments, and is discussed in detail in §4.3.

If there is a defect which can cause the scattering $k \pm q \rightarrow k$, a series of twice scattering, $k \rightarrow k \pm q$ and succeeding $k \pm q \rightarrow k$, may be one of the Raman processes in which one phonon participate. In this process, the condition $q = 0$ is no longer necessary. The intensity of such a process will be generally very weak, but will become recognizable when the intermediate $k \pm q$ state is identical to a real electronic state. Thus the D-band has been assigned to this double resonance Raman scattering. 2) In this explanation of the D-band, only the elastic scattering due to defects is essential, and therefore, a variety of defects can cause similar “D-band”. In spite of that the structure of defects responsible for the D-band in as-grown SWNTs has not yet been fully clarified, the increase of the D-band in the spectra of the $O^+$ irradiated samples is possibly due to scattering by defects that are closely related O atoms. Substitutional O impurities in SWNTs may be candidates for such defects.

4.2 Stability of the substitutional O atom

Due to the ultra-low-energy $O^+$ implantation, we may expect to introduce O impurities substitutional sites, which is a possibility for the cause of the increase of D-band. It is important to know whether or not the substitutional O impurities are stable in the SWNTs. To answer this question, we calculated the electronic energy of the $(6, 0)$ SWNT with a substitutional O atom in a unit cell as the simplest example, by using the first principle pseudopotential method based on the local density approximation. The code used was “OSAKA2000nano”, whose components are described in ref. 9. Atom positions and cell parameters were relaxed in order to obtain the minimum total energy by the conjugate-gradient method under a constant pressure, and a stable structure was obtained as shown schematically in Fig. 4. In the result, the diameter of the tube is approximately 0.5 nm, and the length of the unit cell is approximately $a = 0.417 \text{ nm}$ along the tube. As is shown in the figure, the substitutional O atom is stable if the coordination number is equal to at least 3 in the isolated SWNT.

The three nearest neighbor distances from the O atom at site 0 to the C atoms at sites 1, −1, and 7 are 0.179, 0.178 and 0.166 nm, respectively. These values are approximately 13% greater than that between a C atom distant from a O atom, for example, 0.161 nm between site 6 and sites 5 or −5, and 0.141 nm between sites 6 and 8.

4.3 Resonant Raman spectra

As described in §4.1, it is well known that the Raman spectra of SWNTs in the present excitation region are enhanced by the resonant effects. This is the main reason for the difference between the RBM spectra in Figs. 2 and 3. Various behaviors of the RBM intensities owing to the $O^+$ implantation are probably related to the resonant effects, and thus we discuss these in detail here.

The resonance conditions in the Raman scattering process are illustrated schematically in Fig. 5. Because the incident photon energy $E_i$ is constant in the present experiments, the energy level $E_i$ of the SWNTs is a parameter in this figure.

When $E_i$ is much less than $E_t$ as shown in Fig. 5(a), no real electronic state can affect the process, and therefore, the Raman process only occurs through virtual states. Non-resonant Raman lines due to RBMs are so weak that they cannot be observed in Figs. 2 and 3. As the energy of the electronic state increases to be slightly higher so that $E_i = E_t = \omega$, the photon energy of the Raman scattering light $E_i$ coincides with the transition energy $E_t$, as shown in
is resonant. Finally, in Fig. 5 by the O
change in the energy levels from (c) to (a), or from (c) to (e)
irradiation of the SWNTs. This behavior may be due to the
energy, and the inverse lifetime of 8 meV for the resonant
Stokes lines appear in the resonant Raman spectra. As
Fig. 5(e), and no resonant line is observed, similarly to the
features in Figs. 2 and 3 can be explained as follows. Peaks
in Fig. 3 disappear upon the implantation, but the Stokes line
at approximately 180 cm
1
is still observed in all spectra. The
change from (b) to (a) takes place in the electronic state.

4.4 Band structures of O-doped SWNTs
If the explanation provided in the previous section is
correct with respect to the behavior of Raman spectra, the
electronic states change by more than 28 meV under O
irradiation. The change is so large that it is difficult to accept
that the cause of the change is simply a perturbation from
outside the SWNTs, such as the adsorption of O atoms, for
example. The structure of the SWNT must be modified to a
certain degree by the implanted O atoms. It should be
determined whether the substitutional O impurities are
candidates for the cause of the change in the electronic
states, or not. To estimate the degree of change in the band
structure due to the substitution of O atoms, we calculated
the band structure of SWNTs with O atoms by using a tight-
binding model in which only the electrostatic potential of
periodically doped O atoms is taken into account for
simplicity: that is, the parameters in this model are the on-site
energies $E_{C_0} = 0$ at C sites and $E_O = -5.16 \text{eV}^{11}$ at O
sites, and the transfer energy $T = 3.12 \text{eV}^{11}$ which is
common to all of the nearest neighbor O–C and C–C bonds.
Strain effects induced by O impurities as well as the
difference in the transfer between O–C and C–C bonds are
neglected here, though they should be studied in the future.

Figure 6(a) shows the band structure of a pure (6, 0)
SWNT calculated using the tight-binding model. If one of

Fig. 5. Schematic illustrations of energy levels relevant to resonant
Raman scattering from SWNTs, where $E_i$ indicates the incident photon
energy which is constant in this figure, $E_i$ is the energy of the electronic
state in a SWNT measured from the ground state, $\omega$ is the phonon energy
of RBM, $E_s$ is the photon energy of the anti-Stokes Raman line, and $E_t$ is
the photon energy of the Stokes Raman line. From the energy
conservation rule, $E_s = E_t + \omega$, and $E_t = E_i - \omega$. Solid horizontal lines
indicate real states, while dotted horizontal lines are virtual states. Solid
vertical arrows indicate transitions in the resonant Raman process, while
dashed vertical arrows are nonresonant transitions.

Fig. 5(b). In this case, the resonant Stokes line is expected,
but an anti-Stokes line is not yet observed. When $E_i$ becomes
the same energy as $E_t$ in Fig. 5(c), both Stokes and anti-
Stokes lines appear in the resonant Raman spectra. As $E_i$
increases to be $E_i + \omega$ in Fig. 5(d), only the anti-Stokes line
becomes much higher as shown in
Fig. 5(e), and no resonant line is observed, similarly to the
case of Fig. 5(a).

Taking $\omega \approx 20 \text{meV} (160 \text{cm}^{-1})$ as a typical phonon
energy, and the inverse lifetime of 8 meV for the resonant
scattering process\textsuperscript{10} into account, we can estimate that
the energy difference between (a) and (c) or between (c) and (e)
in Fig. 5 is approximately 28 meV.

On the basis of the resonance conditions, the spectral
features in Figs. 2 and 3 can be explained as follows. Peaks
at approximately $\pm 171, \pm 140, \pm 119 \text{cm}^{-1}$ in Fig. 2, and at
approximately $\pm 117 \text{cm}^{-1}$ in Fig. 3 disappear due to the O
irradiation of the SWNTs. This behavior may be due to the
change in the energy levels from (c) to (a), or from (c) to (e)
in Fig. 5 by the O
irradiation. In this case, the change in the
levels should be greater than 28 meV. On the contrary, peaks
at approximately $\pm 129 \text{cm}^{-1}$ in Fig. 2 and at approximately
$\pm 133 \text{cm}^{-1}$ in Fig. 3 appear upon the O
implantation, and therefore, it is likely that the energy levels are changed from
(a) to (c), or from (e) to (c), in Fig. 5. An interesting case is
that the anti-Stokes line at approximately $-180 \text{cm}^{-1}$ in
Fig. 3 disappears upon the implantation, but the Stokes line
at approximately $180 \text{cm}^{-1}$ is still observed in all spectra.
The explanation may be that the energy level changes from
(c) to (b) in Fig. 5. Another interesting case is that the Stokes
line appears at approximately $160 \text{cm}^{-1}$ in Fig. 3 while the
anti-Stokes line is observed at approximately $-160 \text{cm}^{-1}$ in
all spectra. The change from (d) to (c) is responsible for this
behavior. In the above two cases, the change of level is about
20 meV (that is, the phonon energy). The Stokes peak at
approximately $142 \text{cm}^{-1}$ in Fig. 3 disappears upon the
irradiation, but the anti-Stokes line at approximately
$-142 \text{cm}^{-1}$ is still weakly apparent in all spectra. The
change from (b) to (a) takes place in the electronic state.
the C atoms in a unit cell is replaced by O atoms in the atomic configuration shown in Fig. 4, the degenerated bands in the pure SWNT are split into two bands in the doped SWNT because of the lack of rotational symmetry around the tube direction \( z \), as shown in Fig. 6(b). The splitting is clearly apparent near the zone boundary at \( k_z = 0 \) or \( \pi/a \), where the density of states exhibits van Hove singularities, and the optical transition takes place between such singularities. In Fig. 6(b), typical zone-boundary points are \( 'a' \) at 2.42 eV, \( 'b' \) at 2.29 eV, \( 'c' \) at 1.90 eV, and the optical transition takes place between such singu-
larities. In Fig. 6(b), typical zone-boundary points are

- **a** at 2.42 eV
- **b** at 2.29 eV
- **c** at 1.90 eV

Optical transitions are allowed from \( 'a' \) to \( 'c' \) at 1.87 eV which is near to point \( 'c' \) in Fig. 6(b). The origin of this state will be a certain mixing of bands including points \( 'a' \) and \( 'c' \) in Fig. 6(b). The amplitude of the wavefunction of point \( 'f' \) has a high intensity at site 0 as shown in Fig. 7. This suggests that the band including point \( 'f' \) is an impurity band partially localized around the O atoms, and further, this point may be related to a localized impurity state in the SWNTs with extremely diluted O atoms.

Since the band structures depend on the chirality of the SWNTs, it is necessary to examine the effects of impurities in SWNTs with other chiralities. As an example, Fig. 6(d) shows the band structure of a pure \((6, 6)\) SWNT, and Fig. 6(e) shows that of a \((6, 6)\) SWNT doped with one O atom per four unit cells. Although the concentration of O atoms is 1/96, some bands are separated a few 10 meV from the bands corresponding to the pure SWNT bands, as is evident in the case of the \((6, 0)\) SWNT.

For the above calculations, we choose the \((6, 0)\) and \((6, 6)\) SWNTs as examples since they are simple. Although they are metallic SWNTs, the fundamental points for discussion described above will also hold for semiconducting SWNTs.

The important point is that a small amount of substitutional O impurities may cause a remarkable shift of the transition energies. This effect will qualitatively explain the observed change in the Raman scattering spectra. For the quantitative investigation, we must utilize more precise models that include the strain effects as well as other defects such as the interstitial O impurities, which may induce similar effects.

5. Conclusions

Raman scattering measurements were carried out on SWNTs implanted with ultra-low-energy \( O^+ \) ions. The G/D intensity ratio decreases with the \( O^+ \) irradiation. This signifies that certain defects are introduced to the SWNTs. The intensities of the Stokes and anti-Stokes Raman lines due to RBMs exhibit various behaviors as the \( O^+ \) ions are implanted. On the basis of theoretical calculations it is concluded that the presence of stable substitutional O impurities is the basis for a qualitative explain of the experimental results.

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