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# Radial breathing modes of single-walled carbon nanotubes in resonance Raman spectra at high temperature and their chiral index assignment

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**Abstract**

Radial breathing modes (RBMs) in resonance Raman spectra from single-walled carbon nanotubes (SWCNTs) on a $SiO_2$/Si (0 0 1) substrate are studied between 25 and 720 °C. A change in the relative intensity of each RBM peak with temperature is observed, which originates from the temperature dependence of the resonance condition of nanotubes. For 25 °C, each RBM peak is reasonably assigned on the basis of data in the literature [J. Maultzsch, H. Telg, S. Reich, F. Hennrich, C. Thomsen, Phys. Rev. B 72 (2005) 205438]. By taking into account the temperature-dependent behavior of the relative intensity of the RBM peaks, each RBM peak is successfully assigned even for 720 °C. It is found that most of the observed RBM peaks for a laser excitation energy of $E_{exc}$ = 1.96 eV are from chiral SWCNTs. These results make it possible to discuss further details of the chirality-dependent growth behavior observed for *in situ* Raman spectroscopy.


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*Keywords:* Single-walled carbon nanotubes; Raman spectroscopy; Radial breathing mode

## 1. Introduction

The effective application of carbon nanotubes (CNTs) in electronic devices is highly dependent on our ability to synthesise CNTs with desired chirality, because the electronic structure of CNTs strongly depends on their chirality [1]. To control the growth of CNTs, it is important to clarify their growth mechanism. *In situ* observation of CVD growth using scanning electron microscopy (SEM), transmission electron microscopy (TEM), and Raman spectroscopy is an effective approach to investigate the growth mechanism of CNTs [2–7]. We have succeeded in observing the chirality-selective radial breathing mode (RBM) signals in the resonance Raman spectrum of single-walled carbon nanotubes (SWCNTs) during CVD growth [7].

Resonance Raman spectroscopy is a major technique for assigning the chirality of SWCNTs [8–10]. Recently, on the basis of data obtained in past studies, the chirality assignment of SWCNTs become possible from the resonance Raman spectrum taken with only one excitation energy. However, because the RBM signals observed at CVD temperature show different trends compared to those observed at RT, the SWCNT chiralities corresponding to the RBMs in *in situ* Raman spectra during CVD growth have not been assigned.

In this paper, the RBMs in the resonance Raman spectra of SWCNTs on a $SiO_2$/Si (0 0 1) substrate, taken with a laser excitation energy of $E_{exc}$ = 1.96 eV, is studied between 25 and 720 °C. The change in the relative intensity of each RBM peak with temperature is observed, which originates from the dependence on the resonance condition of nanotubes on temperature. The chiralities of SWCNTs corresponding to the RBMs for 25 °C can be assigned on the basis of data in the literature [10]. Even for 720 °C, the chiralities of SWCNTs corresponding to the RBMs are assigned, taking into account the temperature dependence of the relative intensity of the

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RBM peaks. These results will lead to further discussion about the chirality-dependent growth behavior of SWCNTs observed for *in situ* Raman spectroscopy.

## 2. Experimental

SWCNTs used in this work were synthesized using a CVD system for *in situ* Raman observation [7]. SWCNTs were grown on a $SiO_2$/Si (0 0 1) substrate, on which Co-filled apoferritin (Co-ferritin) as a catalyst was spin-coated [11]. The SWCNT growth was performed at 720 °C for 60 min in a 5-sccm ethanol flow at 0.75 Torr. The *in situ* observation of CVD growth using Co-ferritin catalyst will be reported elsewhere.

Resonance Raman spectra were obtained in a 5-sccm Ar flow at 1.0 Torr using a micro-Raman system (Jobin Yvon HR800) equipped with a single spectrometer (1800 g/mm grating), a holographic notch filter, an optical microscope (50× objective), and a thermoelectrically cooled charge-coupled device (CCD) detector. The sample temperature was monitored by a thermocouple placed under the sample and controlled to be between 25 and 720 °C. In addition, the sample temperature was measured from the temperature-dependent frequency shift of the Si phonon peak at 520 $cm^{-1}$ ($\Gamma_{25'}$) [12]. The temperature monitored by a thermocouple showed a lower value than that obtained from the Si phonon peak. The difference between the two temperatures was estimated to be less than 50 °C. Such a difference was also estimated from the Si phonon peak at 303 $cm^{-1}$ ($2X_3$) [13]. The spectral excitation was provided by a He–Ne laser ($E_{exc}$ = 1.96 eV). The laser power level in a focal spot of 2 μm in diameter was kept below 10 mW to prevent overheating the samples.

## 3. Results and discussion

Fig. 1 shows the RBM signals in the resonance Raman spectrum of SWCNTs on a $SiO_2$/Si (0 0 1) substrate observed at 25 °C. The peaks originating from the substrate are marked with asterisks. This RBM spectrum is fitted with 14 Lorentzian lines. The peak frequency of each RBM is listed in Table 1. Fig. 2 shows an experimental Kataura plot obtained by tunable Raman spectroscopy using HiPCO SWCNTs wrapped with sodium dodecyl sulfate in aqueous solution (SDS-wrapped HiPCO SWCNTs) [10]. The ($n$, $m$) indices in Fig. 2 were determined by comparing the experimental value ($\omega_{RBM}$, $E_{ii}$) with the calculated value ($\omega_{RBM}^{calc}$, $E_{ii}^{calc}$). The $\omega_{RBM}^{calc}$ is determined as:

$$\omega_{RBM}^{calc} = \frac{C_1}{d_T} + C_2, \quad (1)$$

where $d_T$ is the tube diameter derived from ($n$, $m$) index, $C_1$ is a proportional constant, and $C_2$ is an additional constant describing the effects of interaction with the environment (interaction with a substrate or neighboring tubes in a bundle). However, the RBM frequencies for the suspended SWCNTs match well with those for the SWCNTs on $SiO_2$ [14], and also those for the SDS-wrapped SWCNTs [15]. In addition, deviations from the linear dependence of the RBM frequency on the inverse diameter have been predicted for small-diameter SWCNTs

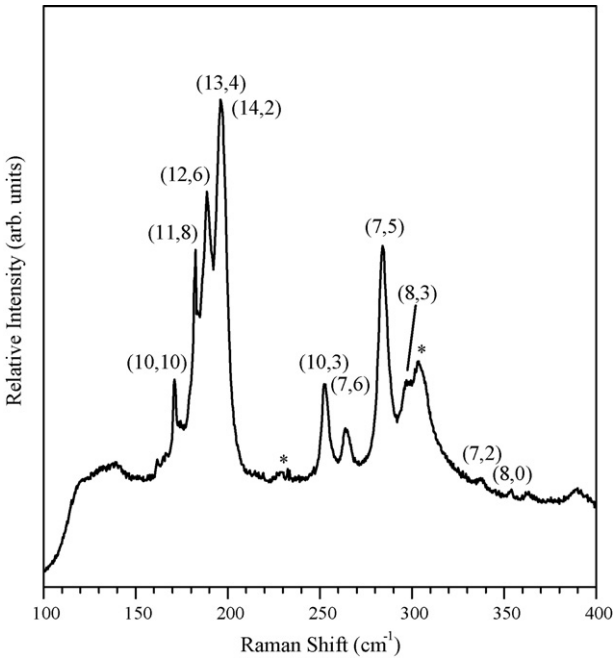


Fig. 1. RBM signals in the resonance Raman spectrum of SWCNTs on a $SiO_2$/Si substrate at 25 °C, taken with a laser excitation energy of $E_{exc}$ = 1.96 eV. The peaks originating from the substrate are marked with asterisks. The assignment of each RBM peak is also shown in the figure.

[16]. For SDS-wrapped HiPCO SWCNTs with tube diameters from 0.7 to 1.2 nm (this is the case in Fig. 2), $C_1$ = 215 $cm^{-1}$ nm and $C_2$ = 18 $cm^{-1}$ are used [10]. On the other hand, $C_1$ = 248 $cm^{-1}$ nm and $C_2$ = 0 $cm^{-1}$ are used for isolated SWCNTs on a $SiO_2$ substrate, with tube diameters from 1 to 3 nm [17]. Such variation of $C_1$ and $C_2$ would originate from the difference in the tube diameter rather than from the environment of the SWCNTs. Although the sample used in this work is composed of SWCNTs on a $SiO_2$ substrate, we have confirmed by atomic force microscopy that most of the SWCNTs are individual ones with the average tube diameter of approxi-

Table 1
Summary of the frequencies of RBM peaks observed at 25 °C ($\omega_{RBM}^{RT}$) and at 720 °C ($\omega_{RBM}^{HT}$) and their assignments

| $\omega_{RBM}^{RT}$ | $\omega_{RBM}^{HT}$ | ($n$, $m$) |
|---|---|---|
| 139 | 138 | |
| 165 | | |
| 172 | | (10,10) |
| 182 | 178 | (11,8) |
| 189 | 185 | (12,6) |
| 195 | 191 | (13,4) |
| 198 | | (14,2) |
| | 200 | (10,7) |
| | 208 | (12,3) |
| | 214 | (13,1) |
| 253 | 252 | (10,3) |
| 264 | | (7,6) |
| 284 | | (7,5) |
| 296 | | (8,3) |
| 337 | 331 | (7,2) |
| 354 | | (8,0) |