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Temperature Measurements of Single-walled Carbon Nanotubes by Raman Scattering

Shohei CHIASHI[†], Yoichi MURAKAMI[†], Yuhei MIYAUCHI[†] and Shigeo MARUYAMA[†]

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1 Introduction

The many unique physical properties of single-walled carbon nanotubes (SWNTs), including heat transfer properties, have been studied in recent years. SWNTs have extremely high thermal conductivity along their axis so that the anisotropy in heat transfer is expected. However, measuring the thermal conductivity of SWNTs is difficult because their structure is very small (the diameter ranges from 1 to 2 nm and the length is more than a few μm).

In this paper, we studied the temperature measurements of SWNTs by Raman scattering as the first step of heat transfer studies of SWNTs. Raman scattering measurement is one of most common analysis techniques for SWNTs samples and physical properties. Three main structures (the G-band, the D-band and radial breathing mode (RBM) peaks) appeared in the Raman spectra of SWNTs. Peak positions (Raman shift), peak widths and peak intensities were measured over a large temperature range, for various SWNTs samples.

2 Experimental

We used four types of SWNT samples. Two SWNT samples were generated by the ACCVD method with zeolites [1] and on a silicon surface. Two additional samples were generated with the laser-oven technique and the HiPco process [2]. In the high temperature range (300~1000 K), Raman scatterings were measured in an atomic force microscope (AFM) chamber with Raman scattering capabilities [3]. The SWNT samples were dispersed or glued on a silicon sample stage. An AC voltage was applied to the silicon sample stage, and Raman scatterings from SWNTs were measured while the temperature was controlled by Joule heating. In addition, the sample was cooled by a helium refrigerator in the low temperature range (4~ 300 K). In order to avoid the oxidation in the high temperature range or the water-condensation in the low temperature range, the sample was kept in vacuum (~10^{-7} Torr) by a turbo-molecular pump. The temperature of the silicon sample stage was not only monitored by a thermocouple but also by the temperature dependence of the Raman scattering of silicon [4].

In Raman scattering measurements, an Ar ion laser (wavelengths of 488.0 and 514.5 nm) and a He-Ne laser (632.8 nm) were used as the Raman excitation laser. Raman scatterings in the high temperature range were measured in a micro-Raman system, and in a macro-Raman system for the low temperature range.

3 Results and Discussions

Fig. 1 shows Raman scatterings from HiPco SWNT samples measured with a 488.0 nm excitation laser at room temperature. The G-band around 1590 cm^{-1}, which comes from SWNTs, was decomposed into sub-peaks according to vibration symmetry of the SWNT. The major peak in the G-band is the G^{+} peak, the peak at the lower frequency to the G^{+} peak is the G^{-} peak and the broad peak around 1530 cm^{-1} is the BWF peak. The D-band around 1350 cm^{-1} shows the existence of defects in the graphitic structure of SWNTs. RBM peaks in the low frequency range (100~400 cm^{-1}) show the tube diameter distribution of the SWNTs. Since this HiPco sample had SWNTs of various diameters and chiralities, many RBM peaks appeared in Fig. 1. We decomposed

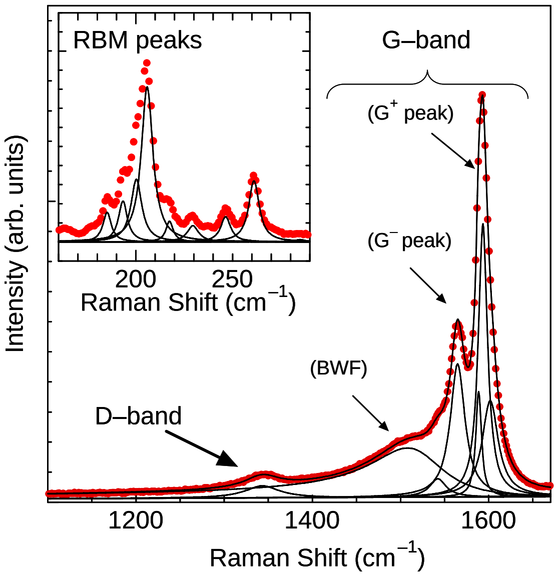

Fig. 1 Raman scattering from HiPco SWNTs.

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* Received : , , Editor :

[†] Department of Mechanical Engineering, The University of Tokyo (7-3-1 Hongo, Bunkyo-ku, Tokyo, 113-8656, JAPAN)

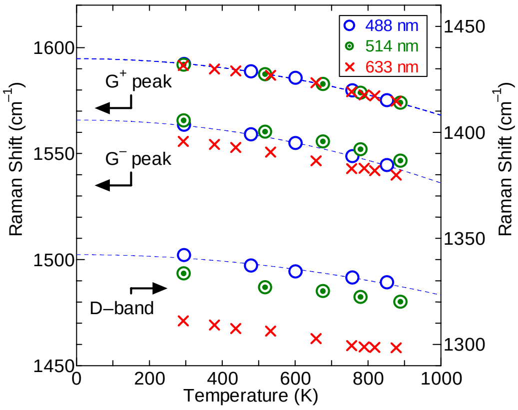

Fig 2 Temperature dependence of Raman shift in the G$^+$, G$^-$ and the D-band peaks.

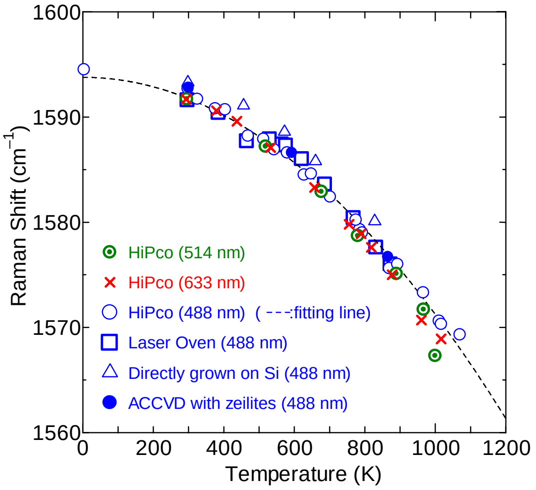

Fig. 3 Temperature dependence of the G$^+$ peak Raman shift in various SWNT samples.

the RBM peaks into Lorentzian curves and analyzed their Raman shifts and peak widths.

Fig. 2 shows the Raman shift temperature dependence of the G$^+$ peak, the G$^-$ peak and the D-band. The sample was HiPco SWNTs and the spectra were measured with three different excitation wavelengths (488.0, 514.5 and 632.8 nm). Generally, Raman scatterings are temperature dependent; namely, a downshift of the Raman shift, peak width broadening and intensity decrease with increasing temperature. In Fig. 2, Raman shifts of three peaks (G$^+$, G$^-$ and the D-band peaks) were downshifted with increasing temperature. The temperature dependence of the G$^+$ peak Raman shift was independent of the excitation laser wavelength, and downshift rates of G$^+$ and G$^-$ peaks were less than that of the D-band.

The temperature dependence of the G$^+$ peak of various SWNTs samples measured with different excitation lasers is shown in Fig. 3. Although the Raman shift of the G$^+$ peak at room temperature varied around 1592 cm^{-1} depending on the SWNT samples, the temperature dependence of the Raman shift was universal for all SWNT samples and excitation wavelengths. It was found that the temperature of the SWNTs could be measured with the Raman shift of the G$^+$ peak.

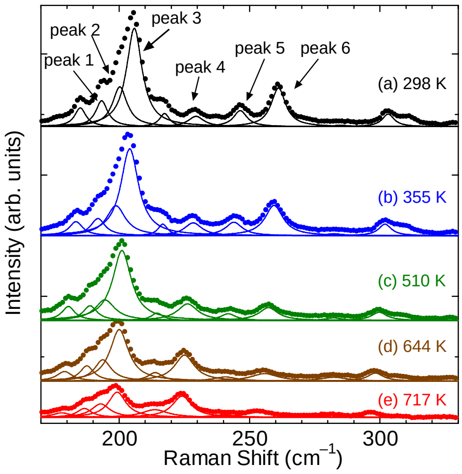

Fig. 4 RBM peak spectra from HiPco SWNTs at different temperatures (488 nm excitation laser)

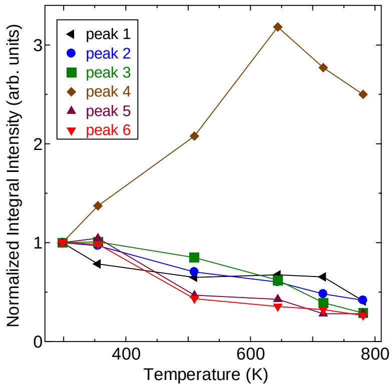

Fig. 5 Temperature dependence of peak intensity in RBM peaks.

RBM peaks from HiPco samples measured at various temperatures are shown in Fig. 4. RBM peaks also showed temperature dependence; with increasing temperature, the Raman shift was downshifted and the peak width increased. Fig. 5 shows the temperature dependence of the intensity of the RBM peaks. Although the intensity of most RBM peaks decreased with increasing temperature, peak 4 (at 229 cm^{-1}, at room temperature) increased. Because RBM peaks were strongly enhanced by resonance Raman effects, this anomaly is attributed to the change in the resonance condition with temperature. This peak intensity was enhanced in high temperature range, but the reason for this drastic change of the resonance condition of this peak remains unclear.

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