TEMPERATURE MEASUREMENTS OF SINGLE-WALLED CARBON NANOTUBES BY RAMAN SCATTERINGS

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INTRODUCTION

The discovery of single-walled carbon nanotubes (SWNTs) [1] has invoked numerous research interests because of their unique physical properties [2] and hence remarkable potential as a new material for various applications. Extremely high thermal conductivity is one of the interesting properties of SWNTs, but because of their small scale, experimental studies of heat transfer involving SWNTs are not easy. In this study, temperature measurements of SWNTs were demonstrated using the temperature dependence of Raman scattering, as the first step of heat transfer studies.

SWNT Raman scattering spectra have three major peaks, which are the G-band (at about 1590 cm^{-1}), D-band (around 1350 cm^{-1}) and the radial breathing mode (RBM, 100-300 cm^{-1}). Previous studies [3, 4] suggested an almost linear decrease of Raman shift in the G-band and RBM with increasing temperature. However, many discrepancies remain in the G-band Raman shifts at higher temperatures, probably because of the laser heating effect and the damage to SWNTs. The reliable measurement of nanotube Raman shift is performed in a wide temperature range with low laser power and in vacuum environment.

EXPERIMENTAL

We recently built an AFM system with Raman scattering measurement capabilities [5]. This experimental apparatus allows the control of the atmosphere and the temperature of samples located on the AFM sample stage. AFM images and Raman scattering can be simultaneously measured under various conditions. Moreover, SWNTs could be successfully generated in this apparatus by the alcohol catalytic CVD method (ACCVD method) [6]. Using this experimental apparatus, the temperature dependence of SWNTs Raman scattering was measured. We prepared 5 types of SWNTs samples, which were generated by the ACCVD method (using zeolite, quartz and silicon as substrates [7]), the laser oven technique [8] and the HiPco method [9]. These SWNTs samples were glued or dispersed onto a silicon wafer, which was connected to an AC power supply and located on the AFM sample stage. In vacuum, an AC voltage was applied to the silicon wafer, and the temperature of the wafer was controlled by Joule-heating while the temperature was monitored using a thermocouple. In the Raman scatterings measurements, an Ar laser (488 nm) was used as the excitation laser. Its power and spot size were 2 mW and about 2 μm, respectively. This

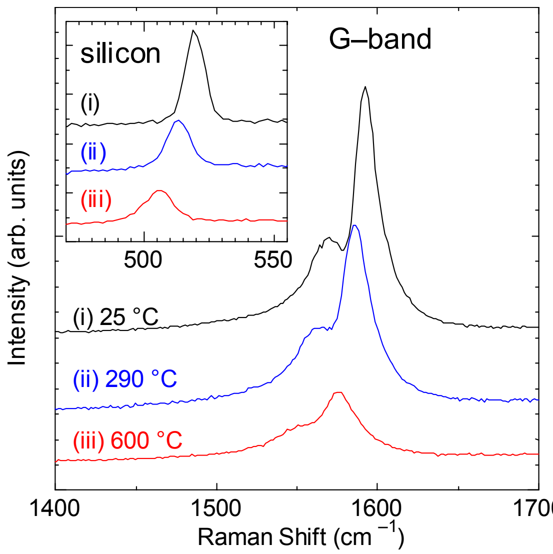

Fig. 1 Raman scattering of SWNTs (ACCVD method) and silicon at different temperatures.

low laser intensity ensured minimal heating of SWNTs.

RESULTS AND DISCUSSION

Fig. 1 shows Raman scattering by SWNTs at different temperatures. This SWNT sample was generated on zeolite using the ACCVD method and dispersed onto a silicon wafer. Raman scattering by silicon has a sharp peak around 520 cm^{-1}. At high temperatures, both the Raman shift and the intensity of the G-band and silicon peaks decreased. The Raman shift downshifted and the intensities decreased in both the G-band and silicon peaks at high temperature.

Fig. 2 shows the relation between temperature and Raman shift in the G-band and silicon peaks. The temperature dependence of the silicon Raman peak was experimentally investigated by Balkanski et al. [10]. They explained the downshift of silicon peak at high temperature by anharmonic effects with three and four phonon interactions in the Raman scattering process, and our present results in Fig. 2 completely agree with their data. In the case of SWNTs samples, the G-band shows almost the same temperature dependence, in spite of different generation methods and morphologies of the samples. The energy balance among the SWNTs, the heated silicon wafer, and the environment (vacuum for this report) determine the temperature of the SWNTs. In this case, the thermal resistance between the SWNTs and the vacuum environment is much larger than that between the heated silicon wafer and the SWNTs, so the temperature of the SWNTs is almost equal to that of the silicon wafer. This is an advantage of making our measurements in vacuum, since the heat transfer to environmental gas may result in a temperature difference between SWNTs and the surface. Furthermore, it should be noted that the SWNTs remain undamaged in vacuum, even above their

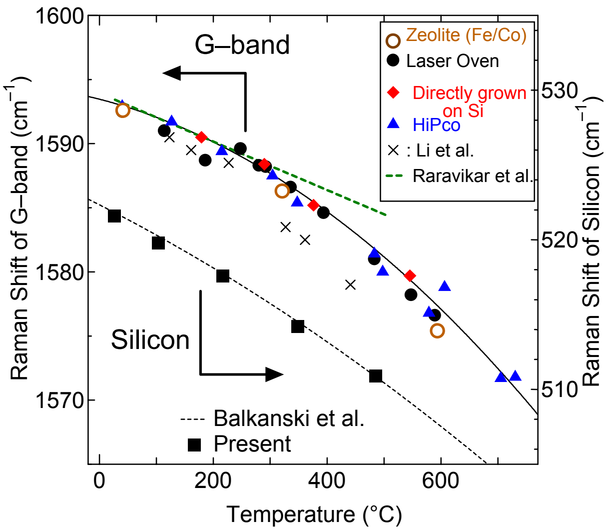

Fig. 2 Effect of temperature on the G-band and silicon Raman peaks

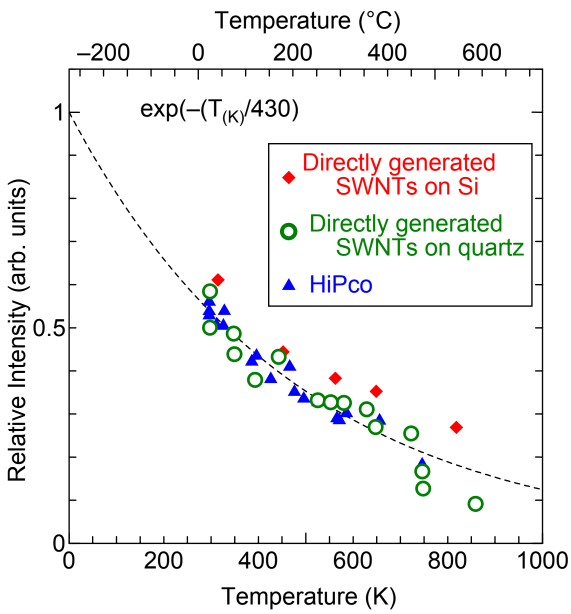

Fig. 3 Temperature dependence of the G-band intensity.

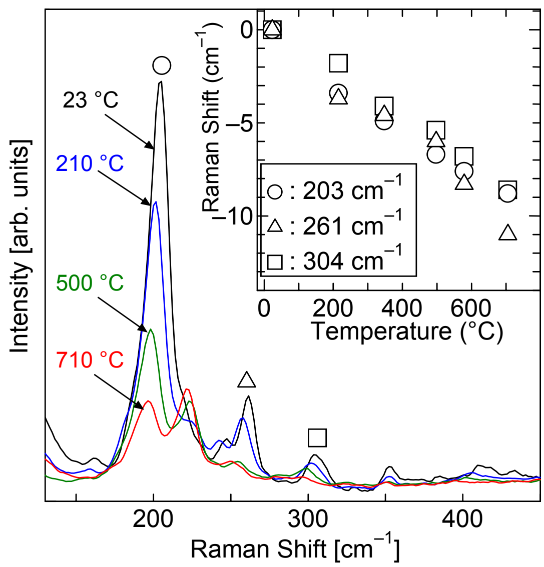

Fig. 4 Raman scatterings of HiPco sample RBM peaks at different temperatures.

burning temperature in air. Using these results we can estimate the temperature of SWNTs from the Raman shift of the G-band.

Fig. 3 shows the temperature dependence of the G-band intensity. The intensity of the G-band exponentially decreased with increasing temperature. Here, data from each sample were fitted to exponential curves as a function of temperature T (K) and normalized at 0 K. In spite of their different generation methods and morphologies of the various SWNTs samples, the temperature dependence of the G-band intensity is the same for all samples, so the temperature of SWNTs can be estimated by the G-band intensity.

RBM peaks also have temperature dependence, shown in Fig. 4. Raman shift of the RBM peaks downshifted and the intensity decreased with increasing temperature. HiPco samples have three major RBM peaks (at 203, 261, 304 cm^{-1}) and each peak has almost the same decrease in Raman shift, as can be seen in the insert in Fig. 4.

CONCLUSIONS

The temperature dependence of Raman shift and Raman relative peak intensity in SWNTs' G-band was measured. The temperature of SWNTs can be determined by the temperature dependence of the G-band Raman shift and its intensity, and the temperature dependence of RBM was also measured.

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