Paper No.

Proceeding of the
1st International Forum on Heat Transfer
November 24-26, 2004, Kyoto, Japan

TEMPERATURE MEASUREMENT OF SINGLE-WALLED CARBON NANOTUBES BY RAMAN SCATTERING DURING THEIR CVD GROWTH

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***Keywords** : Single-Walled Carbon Nanotubes, Raman Scattering, Temperature Dependence.*

ABSTRACT

We generated high-quality single-walled carbon nanotubes (SWNTs) with alcohol catalytic CVD (ACCVD) method in the AFM sample stage, and measured Raman scatterings from the sample during the CVD process. To understand the Raman spectra during the CVD process, we measured Raman scattering spectra from various SWNTs samples at different temperatures (between room temperature and about 700 °C). When the sample temperature increased, both the Raman shift and the intensity of the G-band decreased. Though the comprehensive calibration, the temperature of SWNTs can be measured by using the temperature dependence of Raman shift and the intensity in the G-band. In-situ Raman scattering measurements show that the G-band intensity increased almost linearly with time after an initial rapid increase.

1. INTRODUCTION

The discovery of SWNTs has invoked numerous research interests because of their unique physical properties and hence remarkable potential as a new material for various applications. To realize these applications, the structure control of SWNTs in the generation process is indispensable. Moreover, extremely high thermal conductivity along the tube axis is one of the interesting properties of SWNTs, but because of their small scale, experimental heat transfer studies are difficult. In this study, the real-time Raman scatterings measurements of SWNTs in the growth stage were performed and temperature measurements using the temperature dependence of Raman scattering were demonstrated as the first step in SWNT heat transfer studies.

2. EXPERIMENT

The experimental apparatus is an AFM system (SPI3800N, SPA-300HV, SII) built with Raman scattering measurement capabilities (Chiashi, 2004). AFM images and Raman scattering of samples located on the AFM sample stage can be obtained in situ, and the sample environment can be controlled during measurements.

By using this apparatus, SWNTs were generated by the ACCVD method (Maruyama, 2002), with Raman scattering measurements performed in situ during the CVD process. Iron and cobalt metal particles supported with zeolite particles were dispersed on a silicon wafer. After silicon wafer was heated by Joule-heating in vacuum, ethanol gas was introduced into the chamber at 1.0 Torr and then SWNTs were synthesized.

In order to understand the in-site Raman feature, the temperature dependence of SWNT Raman scattering was measured. We measured 5 types of SWNTs samples, which were generated by the ACCVD method (using zeolite, quartz, and silicon as substrates) (Murakami, 2003), the laser oven technique and the HiPco method. The SWNTs samples were glued or dispersed onto a silicon wafer and the wafer was heated by Joule-heating in vacuum while monitoring the temperature with a thermocouple fixed on the silicon surface. 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 100 μm, respectively. This low laser intensity ensured negligible heating of the SWNTs.

3. RESULTS AND DISCUSSION

Fig. 1 shows Raman scattering spectra from SWNTs on silicon substrate at different temperatures. This SWNT sample was generated on zeolite using the ACCVD method and dispersed onto

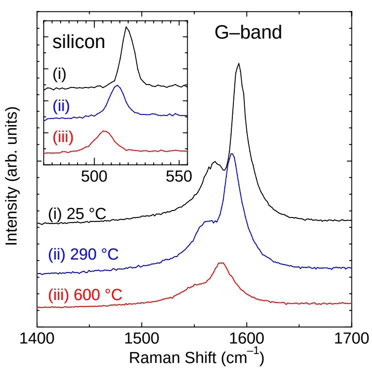

Fig. 1 Raman scattering of SWNTs (ACCVD method) on silicon substrate at different temperatures.

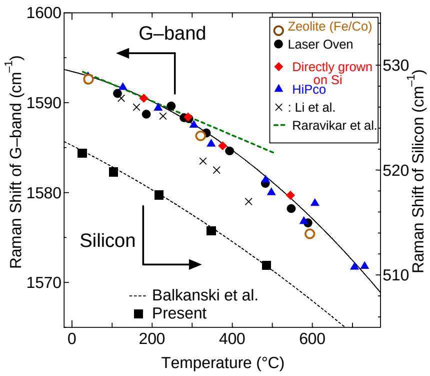

Fig. 2 Effect of temperature on the G-band and silicon Raman peaks.

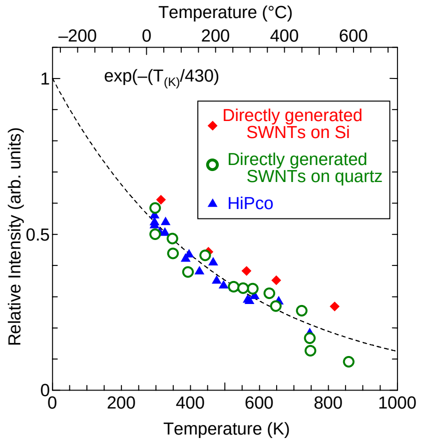

Fig. 3 Temperature dependence of the G-band intensity.

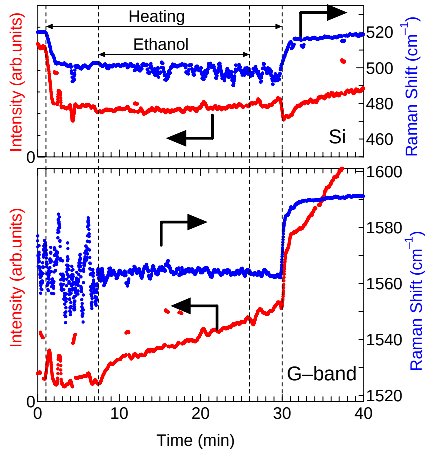

Fig. 4 Real-time Raman scatterings of silicon and the G-band during the ACCVD process.

a silicon wafer. As the temperature increased, both the Raman shift and the intensity of the G-band and silicon peaks decreased, while the width of the peaks increased.

Fig. 2 shows the relation between temperature and the Raman shift in the G-band and silicon peaks. Our data of silicon in Fig. 2 completely agree with the reference data (Balkanski, 1983). The G-band shows almost the same temperature dependence as the silicon peak, despite different generation methods and morphologies of the samples. The energy balance between 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 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 one advantage of making our measurements in vacuum, since the heat transfer to a surrounding gas may otherwise result in a temperature difference between SWNTs and the silicon surface. Furthermore, it should be noted that even above their burning temperature in air the SWNTs remain undamaged in vacuum. Using these results, we can measure 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 decreased exponentially with increasing temperature. Here, data from each sample were fitted to an exponential curve as a function of temperature T (K) and normalized at 0 K. In spite of the different generation methods and morphologies of the various SWNT samples, the temperature dependence of the G-band intensity is the same for all samples. The temperature of SWNTs can be estimated from the G-band intensity also.

The real-time Raman scattering during the CVD process was shown in the Fig. 4. In the case of silicon (the upper side), its Raman shift and the intensity simply changed in response to the silicon temperature. However the G-band is complicated. After heating and the supply of ethanol gas, the G-band appeared around 1560 cm^{-1} and then the intensity increased almost linearly with time. At the beginning of the CVD, the G-band intensity showed an initial rapid increase. The G-band was up-shifted and the intensity increased after heater was turned off, simply because of the temperature dependence.

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