Low temperature effect on Raman and SERS spectra of carbon nanotubes

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1.Introduction

Low-temperature Raman spectroscopy is an interesting technique to investigate molecular vibration by suppressing the thermal interference between the atoms. In particular, although carbon nanotubes (CNTs) has been recognized as an important material in nanotechnologies, Raman analysis of CNTs has been focused only on high temperature [1]. Low-temperature Raman analysis of CNTs has a great potential to reveal molecular vibrational properties of CNTs at low temperature.

In this work, we performed low-temperature Raman analysis of CNTs. We found that the G-band intensity increases, peak width becomes narrower and peak position shifts to higher frequency with decreasing temperature. These changes are in a good agreement with theoretical predictions. Furthermore, we investigated low-temperature effects on surface-enhanced Raman spectroscopy (SERS) of CNTs [2]. One can expect greater enhancements due to the suppression of phonon vibrations in metal. It would be therefore fundamentally important to understand low temperature effects in SERS of CNTs.

2.Result and discussion

For low temperature Raman measurement, we used a home-built cryostat in order to control the temperature of the sample and measured Raman spectra at different temperatures. In our home-built system, temperature of the sample can be decreased down to 123K by using liquid nitrogen, where the heat conducted through a high thermal conductor plate made of copper. This system is combined with a piezo stage so that we can investigate temperature effect of individual CNTs through Raman imaging.

Figure 1 shows Raman spectra of CNTs at different temperatures. Excitation wavelength was 532 nm, laser power at the sample was 10.6 mW, and exposure time was 0.04 seconds. We observed that the width of the G-band peak became narrow, peak position shifted to high frequency and Raman intensity increased as we decreased the temperature. G-band corresponds to the longitudinal optical (LO) phonon mode. The center position and the line width of the LO mode are experimentally found to vary as temperature changes. This variation is due to the anharmonicity in vibrational potential [3,4]. We also confirmed that the experimental results were in a good agreement with theoretical predictions. We then investigated the low temperature effect on SERS. In low-temperature SERS measurements of CNTs, we found out that, in additions to the effects mentioned above, the plasmonic enhancement was also increased due to the suppressed phonon vibrations within the metal. The details of low-temperature SERS will be discussed.

Acknowledgements

The authors would like to acknowledge JSPS Core-to Core program. TU would like to acknowledge to the Grant-in-Aid for Early-Career Scientists 18K14148 and Shorai Foundation for Science and Technology.

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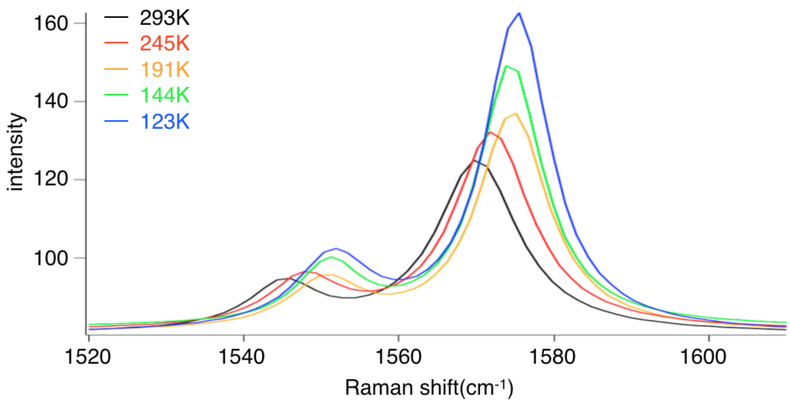

Figure 1. Raman spectra of CNTs for G-band at 5 different temperatures