Evaluation of localized semiconductor to metal transition of semiconducting carbon nanotube by Tip-enhanced Raman investigation

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1. Introduction

Tailoring feature of single walled carbon nanotubes (SWNTs) in property by structure deformation has been an interdisciplinary subject of interest for researchers with an expectation that the control of the electronic property will open an access to new world where nano-circuit and nano-actuator exist and it is quit easy. Recently, drastic change of the properties of crossed SWNTs, for example by bridging them over other SWNTs [1], have received wide-spread attention because a transition from semiconducting state to metallic state was proved to appear only on the junction of crossed semiconducting SWNTs due to $\pi^* - \sigma^*$ hybridization effect, which was theoretically expected since long before [2]. Here, we present a tip-enhanced Raman investigation of extremely localized transition from semiconducting to metal on the junction of crossed SWNTs.

2. Experiment and Results

Preparation of semiconducting SWCNT

In our experiment, semiconducting SWCNTs used for TERS measurements were purchased from Meijo carbon Inc., with a purity of $\sim 99\%$. Individual bundle of this semiconducting SWCNTs with the diameter equal to 1.4 nm were ultrasonically dispersed with 1-2 dichrolethane, then the droplets of this solution were spin-casted onto the glass coverslip to disperse SWNTs appropriately.

Optical setup for tip enhanced Raman microscopy

Our experimental setup, based on an inverted optical microscope combined with a contact-mode AFM, was especially established for TERS microscopy. Silicon cantilever tips used in this measurements were water-oxidized in order to make plasmon resonance shift to the wavelength of light. The cantilever was silver-coated by the vacuum evaporation method and the diameter of the tip apex was set to 15 nm. Raman scattering from the sample was excited by an irradiation of solid state laser (λ : 488 nm) which was radially polarized with the use of eight divided half wavepletes so as to efficiently excite localized surface plasmon polariton along tip apex. The enhanced Raman scattering were detected by CCD incorporated into a Raman spectrometer. By observing the Fano-type breathing of G- mode, which is a Raman signature of metallic behavior of SWNTs, we estimated the local metallization of the semiconducting SWNTs. We found that the metallization was strongly confined to the junction point, as seen from Figs. 1 (a) and (b). This metallization occurs due to the SWNT to SWNT interaction at the junction.

3. Conclusions

Through this study, we can see how the Fano-interaction, which is a Raman signature of metallic behavior, grows up towards the junction point and is localized to a few nanometers in that vicinity. These outcomes could be a great stimulus for a development of nano-electronic devices.



FIG.1. (a) 3D TERS image with the value of 11/ql for an evaluation of metal transition. Planar direction of this image shows x-y topological position of crossed SWCNTs and perpendicular direction to plane, denotes to z-axis, shows 11/ql value. The color shows intensity distribution of TERS spectra at peak position of G-band. (b) Line profile across junction in (a).

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References

[1] T. Hertel et al., Phys. Rev. B. 58, 13870 (1998).

[2] M. S. C. Mazzoni et al., Appl. Phys. Lett. 76, 1561 (2000).