Chirality assignment of individual single-walled carbon nanotubes in carbon nanotube field-effect transistors by micro-photocurrent spectroscopy

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We have proposed a possibility of chirality assignment of individual single-walled carbon nanotubes in nanotube field-effect transistors (FETs) by micro-photocurrent spectroscopy. The nanotube FETs were fabricated by utilizing position-controlled nanotube growth technique using alcohol chemical vapor deposition. Photocurrent signal that originated from a single single-walled carbon nanotube was obtained by using microscopic optical measurement system. A peak was observed at 1.73 eV in the photocurrent excitation spectrum. This corresponds to optical absorption by van Hove singularity of the nanotube with a diameter of ~2 nm. Chirality of the nanotube in the nanotube FET was assigned to be (18, 10) by comparing the experimental results with theoretical calculation. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1650554]

Semiconducting single-walled carbon nanotubes (SWNTs) are promising materials for the nanoscale electron devices such as nanotube field-effect transistors (FETs) for ultrahigh density integrated circuits and quantum-effect devices for novel intelligent circuits, which are expected to make a great breakthrough in the present silicon technology.[1,2] In order to realize such highly functional nanoscale circuits by using SWNTs, there are many issues to be addressed as follows: position control and chirality control of SWNTs, electrode formation to nanotube channels, and so on. In addition to these device fabrication technologies, it is also important to understand device operation based on detailed characterization of nanotube devices. In particular, a study of ''chirality'' of SWNTs in nanotube devices is probably very important because it determines density of states, band gap, and other electronic properties of the SWNTs.

Characterization of nanotube FETs are usually performed by electrical measurement through three terminals. Because semiconducting nanotubes are direct transition semiconductor similar to compound semiconductors, they can emit and absorb photons with high efficiency. Then, characterization of nanotube FETs by using optical measurements would also be possible. The optical characterizations have an advantage because information on energy band structure of the nanotube is obtained by spectroscopic analysis. For example, resonant Raman scattering spectroscopy of SWNTs is one of the most commonly used techniques to assign chiralities of the SWNTs. However, it is difficult to observe Raman signal from a single SWNT because of poor Raman scattering efficiency.

In this letter, we have proposed a possibility of chirality assignment of an individual SWNT in nanotube FETs by microscopic photocurrent (μ-PC) spectroscopy. Nanotube FETs with a single SWNT were fabricated by utilizing position-controlled nanotube growth technique using alcohol chemical vapor deposition (CVD). μ-PC spectroscopy and atomic force microscope (AFM) observation have been performed in the nanotube FETs. Chirality of the nanotube channel was assigned from the μ-PC excitation spectrum by comparing the results with theoretical calculation, the so-called Kataura plot.

The nanotube FETs were fabricated by utilizing position-controlled nanotube growth technique.[3,4] A heavily doped p^+-silicon wafer with thermally oxidized SiO_2 (100 nm) was used as a substrate. Metal catalysts consisting of a double layer of Co (2 nm) over Pt (10 nm) were patterned on the substrate using conventional photolithography and metal lift-off processes. SWNTs were synthesized by thermal CVD. A mixture of ethanol (50 sccm) and argon (100 sccm) was used as a source gas.[5] The total pressure in the furnace was 2 Torr. The growth temperature and time were 900 °C and 1 h, respectively. The device fabrication was completed by Ti/Au electrode formation both on the patterned catalysts and on the back side of the substrate. The back side metal was used as a gate electrode.

A tunable continuous-wave Ti/sapphire laser was used as an excitation source in the present μ-PC spectroscopy. The laser beam was focused on the sample surface by an objective lens ($\times 50$). The diameter of laser spot was ~2 μm. Polarization of the excitation laser was parallel to the axis of nanotube. The device was mounted on a cold finger of a cryostat and cooled down to 10 K.

Figure 1 shows drain current (I_D)−gate-source voltage (V_{GS}) characteristics of nanotube FET in dark (dashed line) and under illumination (solid line). Here, the excitation energy was 1.73 eV, which corresponds to absorption energy of the third interband gap of a van Hove singularity of the nanotube as described later. When the device was illuminated by the laser, the threshold voltage shifted in a direction of nega-

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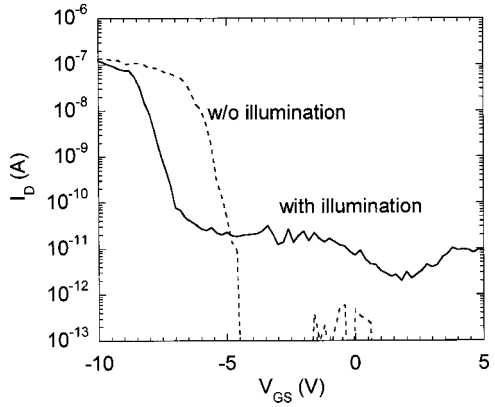

FIG. 1. I_D–V_{GS} characteristics of nanotube FET in dark (dashed line) and under illumination (solid line).

tive V_{GS}, and the I_D at off-state region ($V_{GS} > -5$ V) increased. The threshold voltage shift is probably due to an accumulation of photoexcited electrons at the p-Si/SiO_2 interface. Since, in the off-state region, carriers were not injected from electrodes, the observed drain current would be caused by photoexcited carriers.

Figure 2 shows the photocurrent as a function of position of the laser spot, which was scanned from A to A' shown in the SEM image of the inset. Here, the device was biased at off-state as $V_{DS}=1$ V and $V_{GS}=5$ V. The maximum photocurrent was obtained at $x \sim 27$ μm. There was a SWNT at this position as shown in the SEM image. The dotted line in the figure is a fit by a Gaussian. The photocurrent broadening corresponds to the intensity distribution of laser spot, which is a Gaussian with a deviation of ~ 2 μm.

AFM observation was performed for the nanotube FET where photocurrent was observed. Here, a cantilever with small spring constant (~ 0.1 N/m) was used in noncontact mode AFM in order to minimize a deformation of the SWNT. Figure 3(a) is the AFM image, and Fig. 3(b) is a cross-sectional profile between B and B' in (a). The channel of the present device was determined to be a single SWNT with a diameter of ~ 2 nm. Therefore, observed photocurrent resulted from electron–hole excitation in the single SWNT.

By varying the wavelength of Ti/sapphire laser, the excitation spectrum of μ-PC was obtained. Here, excitation power was set to a condition of constant photon number in the whole wavelength range by using a laser power stabilizer. Figure 4 shows the μ-PC as a function of photon energy. A peak was observed at 1.73 eV. This is probably attributed to optical absorption by the third interband gap of van Hove singularity of the semiconducting SWNT. The linewidth is larger than the width of ideal density-of-state of SWNTs. This might be due to the fact that the electronic band structure was modulated by the effect of the interaction with substrate since the SWNT in the FET contacted with a SiO_2/Si substrate.

Generally, if we know the energy of van Hove singularity and the diameter of a SWNT, it is possible to assign the chirality by comparing with theoretical prediction. Figure 5 shows calculated absorption energies corresponding to van Hove singularities as a function of diameter for various SWNTs, the so-called Kataura plot.[6] Here, the carbon–carbon interaction γ_0 of 2.9 eV was used. From the μ-PC excitation spectrum and the AFM observation, the SWNT in the present nanotube FET had an absorption energy of 1.73

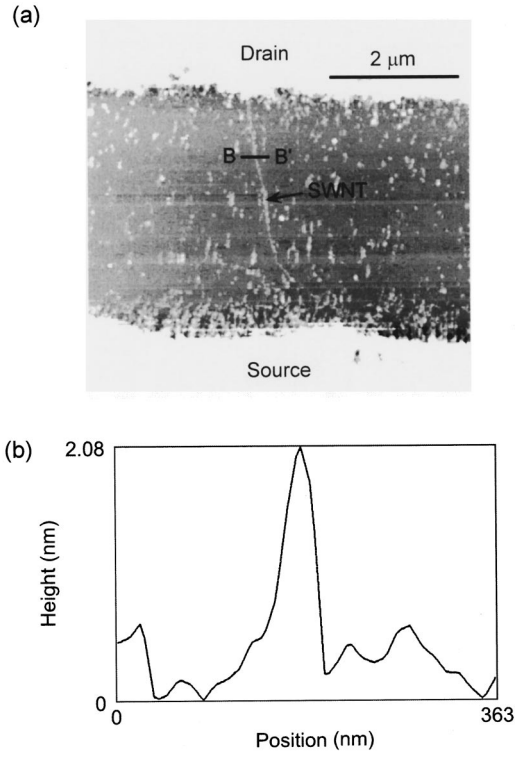

FIG. 3. (a) AFM image at the position where μ-PC was observed in Fig. 2, and (b) cross-sectional profile between B and B'.

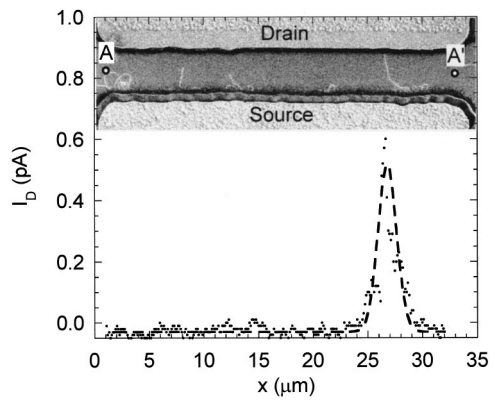

FIG. 2. μ-PC as a function of position between A and A' shown in SEM image of the inset. The dotted line is a Gaussian fit.

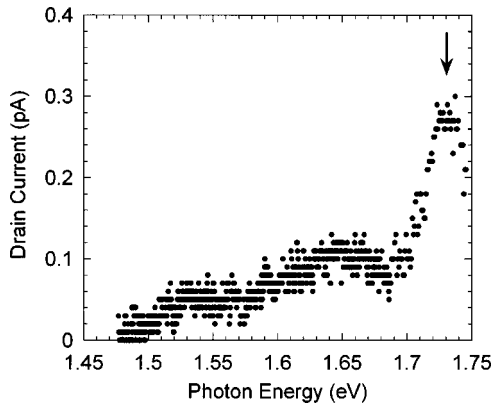

FIG. 4. μ-PC excitation spectrum.

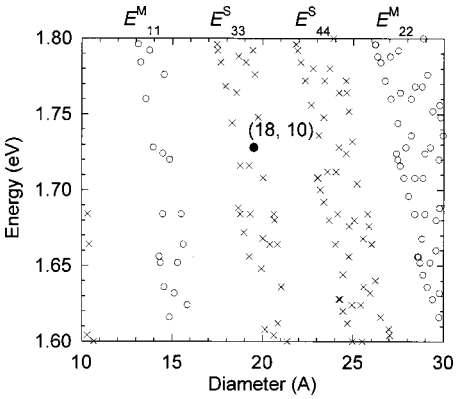

FIG. 5. Kataura plot. Open circles and crosses are metallic and semiconducting, respectively. The chirality of the present nanotube was assigned to be (18, 10) as shown by the dot.

eV and a diameter of ~2 nm. Consequently, the chirality of the SWNT would be assigned to be (18, 10) as shown by a closed circle. The (18, 10) nanotube is semiconducting. This agrees with the FET operation of the device. Any signals could not be detected in micro-Raman scattering spectroscopy of this SWNT FET channel on SiO_2 probably because of poor efficiency of Raman scattering. The present μ-PC spectroscopy has an advantage of high sensitivity over micro-Raman scattering spectroscopy in assigning chiralities of SWNTs in nanotube FETs.

A broad peak was also observed at 1.64 eV even though the (18, 10) SWNT does not have any van Hove singularities at the energy region. Even though the origin of this peak is not clear, it might be a phonon replica of the peak at 1.73 eV. Elucidation of the origin of the broad peak will be a subject of further investigation.

In summary, we have observed μ-PC in an individual SWNT channel in a nanotube FET, which was fabricated by utilizing position-controlled nanotube growth. A peak was observed at 1.73 eV in the μ-PC excitation, which was attributed to optical absorption by a van Hove singularity. A possibility of chirality assignment of the SWNT in the nanotube FET was suggested.

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[1] C. Dekker, Phys. Today **52**, 22 (1999).
[2] M. S. Dresselhaus, G. Dresselhaus, and P. Avouris, *Springer Series, Carbon Nanotubes* (Springer, Berlin, 2001), Vol. 80.
[3] H. T. Soh, C. F. Quate, A. F. Morpurgo, C. M. Marcus, J. Kong, and H. Dai, Appl. Phys. Lett. **75**, 627 (1999).
[4] Y. Ohno, S. Iwatsuki, T. Hiraoka, T. Okazaki, S. Kishimoto, K. Maezawa, H. Shinohara, and T. Mizutani, Jpn. J. Appl. Phys., Part 1 **42**, 4116 (2003).
[5] S. Maruyama, R. Kojima, Y. Miyauchi, S. Chiashi, and M. Kohno, Computer **360**, 229 (2002).
[6] S. Maruyama, http://www.photon.t.u-tokyo.ac.jp/~maruyama/kataura/kataura.html