Extended Abstracts of the 2007 International Conference on Solid State Devices and Materials, Tsukuba, 2007, pp. 694-695

P-13-3

Band-Gap Tuning of an Individual Single-Walled Carbon Nanotube with Uniaxial Strain

Hideyuki Maki[1], Tetsuya Sato[1], and Koji Ishibashi[2]

[1]Department of Applied Physics and Physico-Informatics, Faculty of Science and Technology, Keio University, Hiyoshi, Yokohama 223-8522, Japan
Phone: 045-566-1643, E-mail: maki@appi.keio.ac.jp
[2]Advanced Device Laboratory, The Institute of Physical and Chemical Research (RIKEN)
2-1, Hirosawa, Wako, Saitama 351-0198, Japan

1. Introduction

Single-walled carbon nanotubes (SWNTs) are attractive material for the building block of electronic and optical nanodevices, because of their extremely small diameter and the various electronic states. The emission energy obtained from photoluminescence (PL) and electrically induced optical emission is determined by the band gap that depends on the chirality of SWNT. It was theoretically studied that the band gap is varied by the strain of SWNT and the change of the band gap depends on their chirality and deformation mode.[1] Experimentally, there are some reports that the emission energy of PL is shifted due to the strain applied by temperature change or drying of the surfactant suspended or polymer mixed SWNT.[2] In their reports, the chiralities of SWNTs is assigned from the PL spectra of an ensemble of SWNTs and the chirality dependence of the band gap change is investigated. In our study, we have fabricated the new devices for applying strain to the individual suspended SWNTs. Using this device, the processes of the deformation under stretching have been directly observed by a scanning electron microscope (SEM). From the PL measurement for the individual SWNT, the emission energy shift due to the band gap change caused by the elastic strain is observed.

2. Experimental Procedures

Figure 1(a) shows schematic pictures of a device for applying stretch to the suspended SWNTs. SWNTs were grown on a SiO_2/Si substrate by chemical vapor deposition using ethanol and Co catalist at 800 °C, and suspended SWNTs were formed over the crack of the substrate. One side of the crack is opened; therefore, the gap of a crack can be changed by applying extension force for a substrate. The other side is terminated by a slit formed perpendicular to the crack. The crack and slit were induced with a diamond saw. In this device, a stacked piezoelectric device is used as the source of extension. Two L-shaped fittings are glued to both sides of the piezoelectric device, and the substrate with the suspended SWNTs was glued onto the L-shaped fittings. Extension can be directly applied to the suspended SWNTs by applying piezo voltage (V_{piezo}) to the piezoelectric device, because the L-shaped fittings are glued only at both side of the piezoelectric device. The gap extension is ~25 nm/V_{piezo}. This device has very small size (maximal length of ~7 mm); hence it is easy to insert this device into

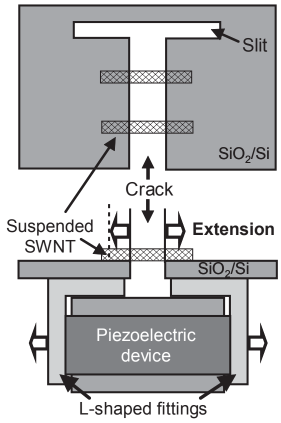

Fig. 1. Schematic top view and cross-section of the fabricated device for applying strain to the suspended SWNTs.

various experimental instruments. In this study, the form of individual SWNT under stretching was directly observed by SEM under applying piezo voltage. In addition, PL spectra from individual SWNTs under stretching were also measured using microscope objective at room temperature in air. For excitation, a HeNe laser (632.8 nm) was used. The PL measurements are on different nanotubes than the SEM observations. PL measurements and SEM observation were carried out around the open side of the crack.

3. Results and Discussions

The form of suspended individual SWNTs under stretching with piezoelectric devices is observed by SEM. One of the results is shown in Figure 2. At V_{piezo} = 0 V, slack SWNT suspended over a crack is observed. By increasing V_{piezo}, however, the gap of crack is extended, and the form of the SWNT gradually becomes straight. Over V_{piezo} = 20 V, the SWNT has straight-line form, and are stretched. During stretching, it is observed that the contact position between the suspended SWNT and Si substrate is varied as indicated by A, B and C in Figure 2. This is due to weak contact between the SWNT and Si substrate. The schematic explanation of the contact position variation is shown in the right side of Figure 2. On the right-hand substrate, the curved SWNT lies on the substrate. During stretching of the suspended SWNT, the SWNT lying on the substrate is drawn by the suspended SWNT, because the contact between the SWNT and the substrate is weak; therefore, the contact position is varied as shown in sche-

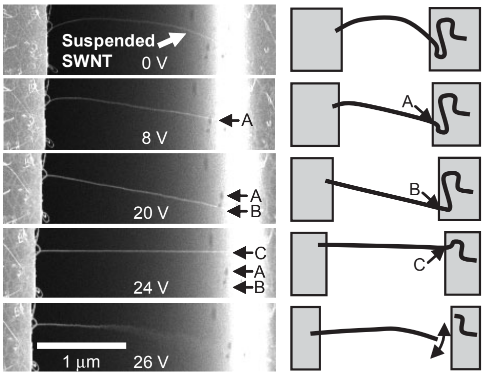

Fig. 2. Left picture: Example of SEM images of the suspended SWNT under stretching with the piezoelectric device. Indicated voltage is the applied V_{piezo}. The contact position between the suspended SWNT and Si substrate is indicated by A, B and C. Right picture: The schema of the suspended SWNT under stretching.

matic picture of Figure 2. At V_{piezo} = 26 V, the right-side of the SWNT are broken or slipped off, and the vibration is observed at the free side of the SWNT. From our many results of the SEM observations, both of "breaking" and "slipping" were often simultaneously observed; therefore, it is not clear whether the right-side of the SWNT in Figure 2 is broken or slipped off.

In this study, we have measured PL from the suspended individual SWNTs under stretching. Figure 3a shows the V_{piezo} dependence of the PL spectra for the SWNT which have emission energy around 1.125 eV. As applied V_{piezo} is increased, the emission peak is shifted toward lower energy. Moreover, the peak goes back to the normal position, when the applied V_{piezo} is reduced to 0 V following application of V_{piezo} = 39 V. Figure 3b shows the V_{piezo} dependence of the emission energy. The emission energy is linearly shifted toward lower energy in the range from V_{piezo} = 15.0 to 32.4 V (region II). This shift can be understood by the band gap narrowing due to uniaxial strain. In the previous study[1], it was reported that uniaxial strain causes the band gap change, whose value depends on the chirality of the SWNT. The band gap change (ΔE_g) under small uniaxial strains (σ) is given by

$$\Delta E_g = \mathrm{sgn}(2p + 1)3t_0(1 + \nu)\sigma\cos3\theta, \qquad (1)$$

where $t_0 \approx 3.0$ eV and $\nu \approx 0.2$ are the carbon-carbon transfer integral and Poisson's ratio, and θ is the chiral angle of the SWNT. p = -1, 0, or 1 is obtained from $n - m = 3q + p$, where n and m are the chiral vector indices and q is an integer. In comparison to the (n,m) indices assignment in previous reports[2,11], reasonable assignment for sample A is (9,4) SWNT species, taking into account the emission energy of 1.125 eV. The (9.4) SWNT has p value of -1; therefore, ΔE_g has negative value from the calculation of Eq. 1: the band gap is narrowed by stretching strain. For the experimental result, the band gap narrowing is observed under stretching; therefore, the assignment of (9,4) indices is consistent with the experimental result for sample A. From Eq. 1, it can be calculated that $\Delta E_g / \sigma$ = -65.9 meV/% for the (9.4) SWNT. On the other hand, from the slope of

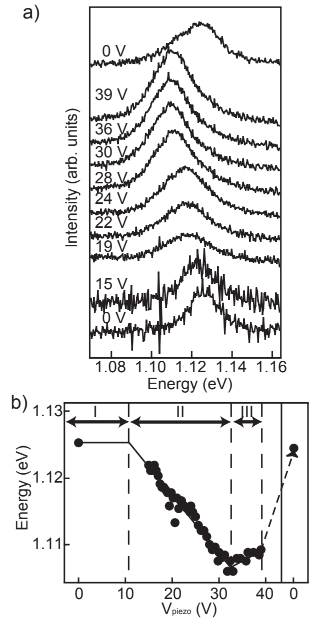

Fig. 3. a) V_{piezo} dependence of the PL spectra for sample A. The applied V_{piezo} is reduced to 0 V after application of V_{piezo} = 39 V. b) V_{piezo} dependence of the emission energy. I, II and III indicate the regions where the behaviors of the emission energy shift are different. Solid lines show the line fittings in each region.

emission energy v.s. V_{piezo} in region II of Figure 3b, it is estimated that $\Delta E_g / \sigma$ = -0.7 meV/%, assuming that the SWNT extension corresponds to the extension of the piezoelectric device. The value of -0.7 meV/% obtained from the experiment is very small compared with that of -65.9 meV/% obtained from Eq. 1. This is because the gap extension of the substrate crack does not directly transmit to the strain of the suspended SWNT. In fact, the SWNT lying on the substrate is slid during stretching of the suspended SWNT. Therefore, the applied strain of the suspended SWNT is very small compared to the strain expected from the gap extension of the substrate. Obtained maximal energy shift and strain are 19.4 meV and 0.3 %, respectively.

The extrapolated line fitted in region II toward low V_{piezo} does not pass through the observed emission energy at V_{piezo} = 0 V; therefore, a region, where the emission peak is hardly shifted during stretching, exists at lower V_{piezo} region (indicated by region I in Figure 3b). In region I, the strain is hardly applied to the suspended SWNT because the suspended SWNT is slack. Moreover, when the applied V_{piezo} is subsequently returned to 0V after application of V_{piezo} = 39V, the emission peak is returned to the normal position due to the relaxation of strain. This result indicates that the emission peak shift is caused by the elastic strain of the SWNT.

References

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