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Direct Observation of the Deformation and the Band Gap Change from an Individual Single-Walled Carbon Nanotube under Uniaxial Strain

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ABSTRACT

We have fabricated a new device for applying uniaxial strain to an individual suspended SWNT, and the form and the photoluminescence (PL) of an individual suspended SWNT under stretching are investigated. The processes of deformation and break of a SWNT under stretching are directly observed by scanning electron microscopy (SEM). From the PL measurements, the emission energy shifts due to the band gap change are measured under the elastic strain. The behaviors of the emission shifts can be related to the deformation processes observed by SEM. Moreover, the emission intensity reduction due to the elastic strain of a SWNT is also observed just before breaking.

Single-walled carbon nanotubes (SWNTs) are attractive materials for the building blocks of electronic and optical nanodevices because of their extremely small diameter and the various electronic states. The emission energy obtained from photoluminescence (PL)[1−6] and electrically induced optical emission[7−9] 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.[10,11] Experimentally, it was reported that the conductance variation of the suspended SWNT is measured under stretching applied with an atomic force microscope tip and is explained by the band gap change due to the strain of the SWNT.[12,13] On the other hand, 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.[14−16] 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).[17] 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. Moreover, the emission intensity reduction due to the elastic strain of the SWNT is also observed just before breaking.

Figure 1a illustrates the cross section of the fabricated device for applying strain to the suspended SWNTs. In this device, two L-shaped fittings are bonded to both sides of the stacked piezoelectric device, which extends uniaxially. On two L-shaped fittings, thermally oxidized Si substrate with suspended SWNTs extending over the crack of the Si substrate is bonded. The crack was induced by cutting from the back of Si substrate with a diamond saw and has the gap of ∼1−5 μm. One side of the crack is open (Figure 1b), therefore, the gap of the crack can be freely opened, and the gap expansion around the open side almost corresponds to the piezo expansion. The other side of the crack is terminated by the slit formed perpendicular to the crack to avoid separation of two substrates on both sides of the crack. This slit was also formed with a diamond saw. The suspended SWNTs were grown by chemical vapor deposition using ethanol at 800 °C for 10 min with cobalt catalysts. As shown in Figure 1b, on the Si substrate, a large number of SWNTs is grown, therefore, the root of a suspended SWNT is often entangled in other SWNTs. However, around the center of suspended SWNTs, many individual SWNTs

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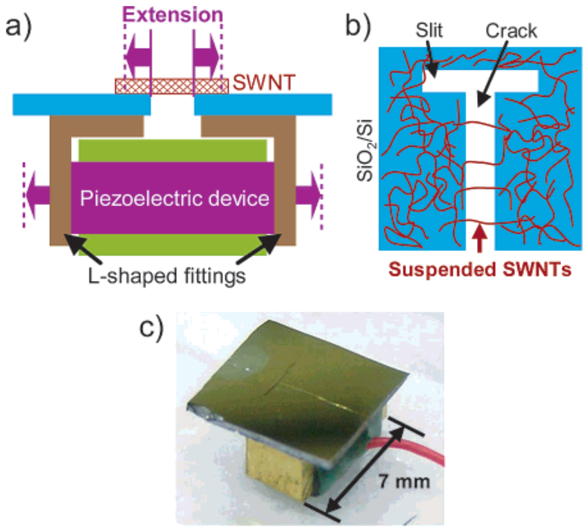

Figure 1. (a) Schematic cross-section of the fabricated device for applying strain to the suspended SWNTs. (b) Thermally oxidized Si substrate, on which suspended SWNTs extending over the crack of Si substrate are grown by CVD. One side of the crack is open, and the gap of the crack can be freely opened. The other side of the crack is terminated by the slit formed perpendicular to the crack. (c) The picture of the fabricated device. The length of the device is approximately 7 mm.

existed because SWNTs with very small diameter can usually be observed by SEM. In this device, a strain can be applied to suspended SWNTs by applying piezovoltage (V_{piezo}) to piezoelectric devices. The extension of piezoelectric device can be directly transmitted to the gap of crack because the L-shaped fittings are bonded only at both sides of the piezoelectric device. The gap extension is ~25 nm/V_{piezo}. The picture of the fabricated device is shown in Figure 1c. The size of this device is very small (maximal length of ~7 mm), therefore, this device can be easily inserted into various experimental instruments such as SEM, optical measurement systems, and electric measurement systems. In this study, the form of individual SWNT under stretching was directly observed by SEM under application of piezovoltage. In addition, PL spectra from individual SWNTs under stretching were also measured using a 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.

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. Slack indicates that the suspended SWNT is longer than the width of the crack and the SWNT has curvature.[18−20] 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 is 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

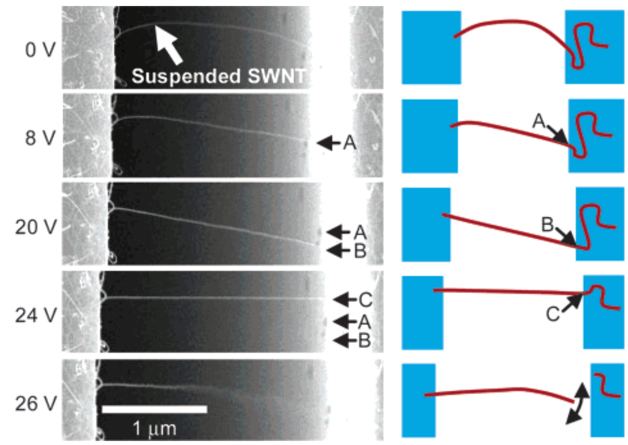

Figure 2. Left picture: Example of SEM images of the suspended SWNT under stretching with the piezoelectric device. Indicated voltage is the applied V_{piezo}. The contact position between the suspended SWNT and Si substrate is indicated by A, B, and C. Right picture: The schema of the suspended SWNT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

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 the schematic picture of Figure 2. At $V_{piezo} =$ 26 V, the right-side of the SWNT is 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 "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 (sample A), which have emission energy around 1.125 eV. As applied, V_{piezo} is increased and the peak width is not changed under stretching; however, 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 $V_{piezo} = 15.0{-}32.4$ V (region II). This shift can be understood by the band gap narrowing due to uniaxial strain. In the previous study,[8] 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

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

where $t_0 \approx 3.0$ eV and $\nu \approx 0.2$ are the carbon−carbon transfer integral and Poisson's ratio[11,12] and θ is the chiral angle of the SWNT. $p = -1$, 0, or 1 is obtained from

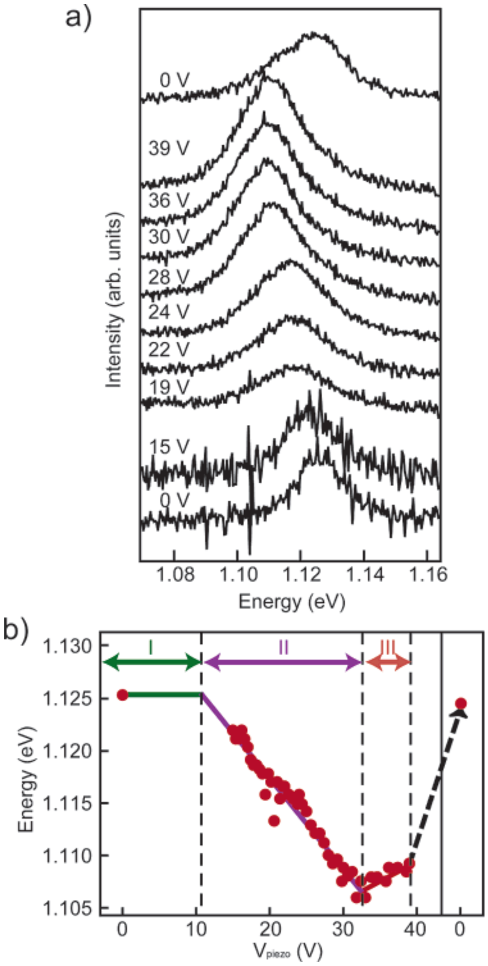

Figure 3. (a) V_{piezo} dependence of the PL spectra for sample A. The applied V_{piezo} is reduced to 0 V after application of $V_{piezo} = 39$ V. (b) V_{piezo} dependence of the emission energy. I, II, and III indicate the regions where the behaviors of the emission energy shift are different. Solid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

$n - m = 3q + p$, 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 of sample A, 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 emission energy vs 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 (using the SWNT length of 2 μm, which is the width of the gap, and extension of 25 nm/V_{piezo}). 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, as mentioned above, the SWNT lying on the substrate is drawn by the suspended SWNT during stretching of the suspended SWNT (as shown in Figure 2). Therefore, the applied strain of the suspended SWNT is very small compared to the strain expected from the gap extension of the substrate. For sample A, obtained maximal energy shift and strain are 19.4 meV and 0.3%, respectively. The emission intensity is increased during stretching. This reason is not clear from this measurement, but there is a possibility that the E_{22} energy is changed by the strain and the resonance between the E_{22} energy and the excitation energy is enhanced. However, photoluminescence excitation (PLE) measurement is needed to argue this mechanism.

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; this corresponds to the case shown in the $V_{piezo} = 0-8$ V of Figure 2. On the other hand, over $V_{piezo} = 32.4$ V, the emission peak is slightly shifted toward higher energy. This reason is not clear, but there is possibility that the strain of suspended SWNT is decreased due to the slip at the contact between the suspended SWNT and the substrate. Moreover, when the applied V_{piezo} is subsequently returned to 0 V after application of $V_{piezo} = 39$ V, 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.

Figure 4a shows the V_{piezo} dependence of the PL spectra for the SWNT (sample B), which have emission energy around 0.861 eV. The emission peak shift is observed as increasing applied V_{piezo}. However, over $V_{piezo} = 17.0$ V, the peak position suddenly returns to high emission energy and the emission energy is hardly varied at higher V_{piezo}. In addition, after the subsequent reduction of V_{piezo} to 0 V, the peak position keeps at same emission energy. Figure 4b shows the V_{piezo} dependence of the emission energy for sample B. In the low V_{piezo} range from 0 to 8.0 V (indicated by region I in Figure 4b), the emission energy is gradually shifted toward low energy. On the other hand, in the V_{piezo} range from 8.0 to 16.0 V (indicated by region II in Figure 4b), the peak position is drastically shifted toward low energy. The origin of these behaviors of the emission peak position in region I and II are the same as sample A: in region I, the strain is hardly applied due to slack of suspended SWNT; however, in region II, the strain is effectively applied due to stretching the SWNT and the band gap is narrowed. From the slope in region II, it is estimated that $\Delta E_g/\sigma = -2.9$ meV/% using the SWNT length of 5 μm, which is the width of the gap. At $V_{piezo} = 17.0$ V, the strain is relaxed and the emission energy is suddenly shifted to high energy, which is nearly normal position. At higher V_{piezo} (region IV) and subsequent 0 V, the energy shift is not observed. This relaxation is possibly due to application of strain through more than one SWNT. Figure 5 shows the SEM images, which shows the state of stretching through two SWNTs. In these images, one SWNT (SWNT no. 1) is stretched through the other SWNT (SWNT no. 2). However, at $V_{piezo} = 6$ V,

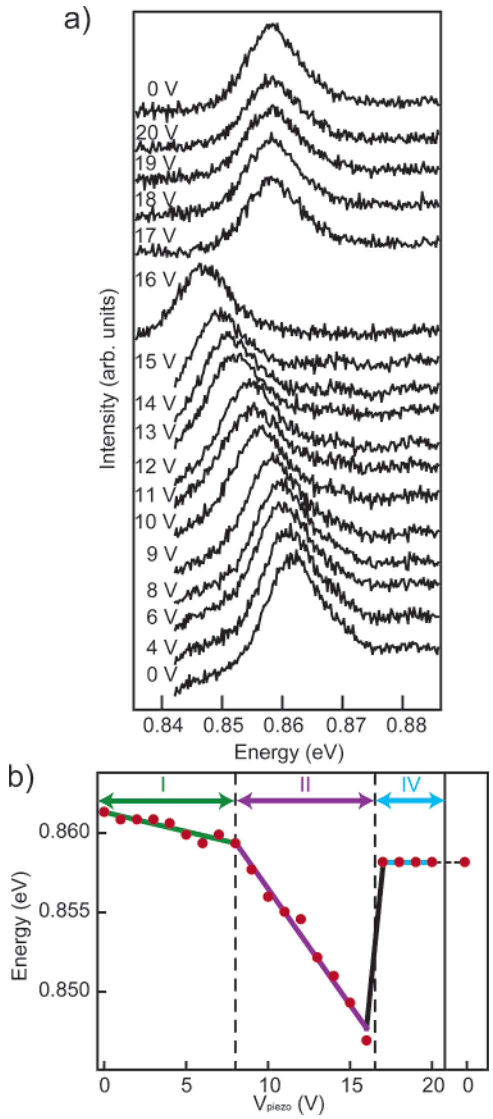

Figure 4. (a) V_{piezo} dependence of the PL spectra for sample B. The applied V_{piezo} is reduced to 0 V after application of $V_{piezo} = 20$ V. (b) V_{piezo} dependence of the emission energy. I, II, and IV indicate the regions where the behaviors of the emission energy shift are different. Solid lines show the line fittings in each region.

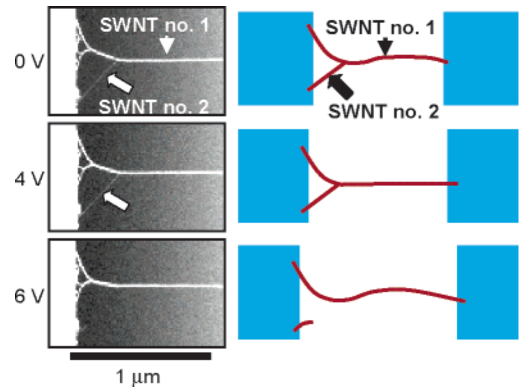

Figure 5. Example of SEM images under stretching through two SWNTs (SWNTs nos. 1 and 2). Indicated voltage is the applied V_{piezo}. SWNT no. 1 is stretched through SWNT no. 2. At $V_{piezo} =$ 6 V, the SWNT no. 2 is broken, and the strain for the SWNT no. 1 is relaxed. The SWNT no. 1 has large diameter; therefore, this SWNT is an individual SWNT with a large diameter or bundled SWNTs, however, they cannot be distinguished from this image.

the SWNT no. 2 is broken (or slipped off), and the strain for the SWNT no. 1 is relaxed. There is a possibility that the strain relaxation in the region IV of sample B is caused by this mechanism.

For another sample (sample C), the variation of not only the emission energy but also the emission intensity is observed just before the breaking of the SWNT. Figure 6 shows the V_{piezo} dependence of (a) PL spectra, (b) emission energy, and (c) emission intensity for sample C. In this measurement, after V_{piezo} is applied from 0 to 8.3 V, V_{piezo} is returned to 8 V and then is finely increased again. The emission energy is slightly shifted toward lower energy in the range of $V_{piezo} = 0-3$ V (region I) and is greatly shifted in the range of 3−6 V (region II) and then is slightly shifted toward higher energy in the range of 6−8 V (region III). These behaviors of the emission energy in region I, II, and III for sample C are similar to that for sample A shown in Figure 3. In these regions, the emission intensity is hardly varied, as shown in Figure 6c. However, over $V_{piezo} = 8$ V (region V), the emission intensity is drastically decreased as V_{piezo} increases and takes minimum value at 8.3 V. However, the emission intensity is recovered by reduction of applied V_{piezo} to 8.0 V, and then the intensity is decreased again as V_{piezo} increases finely. This recovery indicates that the intensity reduction is due to the elastic strain of the SWNT. The mechanism of the intensity decrease under the elastic strain is not clear, however, two possibilities of the mechanism might be proposed. One is the increase of nonradiative relaxation due to large elastic deformation of SWNT structure. If the large deformation of the SWNT structure is locally induced by the large strain, there is possibility that the electronic structure of SWNT fluctuates, depending on the position of the SWNT, and the nonradiative relaxation is increased. The other is the displacement of resonant energy due to the large change of the E_{22} van Hove singularity. The strain induces the change of not only the band gap (E_{11}) but also the E_{22} energy. The E_{22} energy change might cause the reduction of excitation efficiency. In region V of Figure 6b, the emission energy shift ($\Delta E_g/\sigma = -2.3$ meV/%) is observed; therefore, the E_{22} energy is possibly also changed. However, it is unlikely that a shift in E_{22} causes such a large drop in intensity because of the small shift in E_{11}. Further experiment, such as PLE measurement, is needed to argue the mechanism of the intensity reduction. The emission peak is disappeared at $V_{piezo} = 8.305$ V and cannot be observed after subsequent V_{piezo} reduction to 0 V. This is because the SWNT broken by the large stretching is bent into the crack and the suspended SWNT has disappeared. The disappearance of the suspended SWNT broken (or slipped off) by the stretching is often observed by SEM measurement, as indicated in Figure 7.

In comparison to the chirality assignment in previous reports, the speculated chirality assignment of sample B and C is (15,1) or (14,3), taking the emission energy (0.86 eV) of these samples into account. Both of these chiralities take $p = -1$ in eq 1, therefore, the ΔE_g calculated from eq 1 takes a negative value. This result corresponds to the results

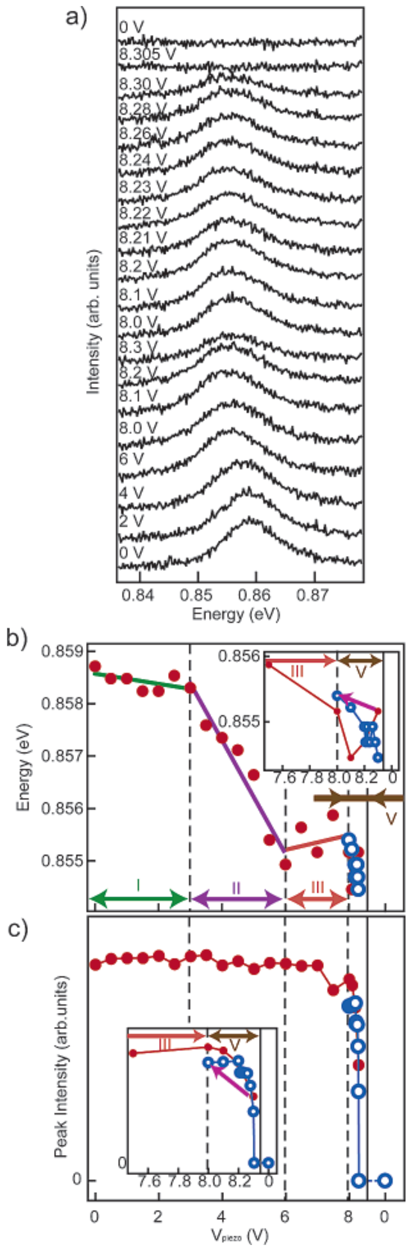

Figure 6. (a) V_{piezo} dependence of PL spectra for sample C. In this measurement, after V_{piezo} is applied from 0 to 8.3 V, V_{piezo} is returned to 8 V and then is finely increased again. (b and c) V_{piezo} dependence of emission energy and emission intensity, respectively. I, II, III, and V indicate the regions where the behaviors of the emission energy shift are different. Magnified emission energy and intensity around region V is shown in the insets of (b) and (c). Open circles are the measurement results at finely increased V_{piezo} after V_{piezo} is returned from 8.3 to 8 V. The arrows in the insets indicate the change of V_{piezo} from 8.3 to 8 V. The peak intensity indicates the count at the peak after background subtraction.

of Figure 4 and 6. However, E_{22} energies of (15,1) and (14,3) SWNTs (approximately 1.3 eV) are quite different from the excitation energy (HeNe laser: 1.959 eV), therefore, their chiralities cannot be accurately determined. In this study, the only band gap narrowing is observed. If the PL measurements under stretching are carried out for the SWNT with $p = 1$ of eq 1, the band gap widening will be observed. Taking the excitation energy into account, the SWNT with the emission energy of 0.90 [chirality: (12,2)], 0.99 [(10,3)], 1.11[(7,6)], and 1.27 eV [(6.5)] takes $p = 1$, as indicated in refs 2 and 14.

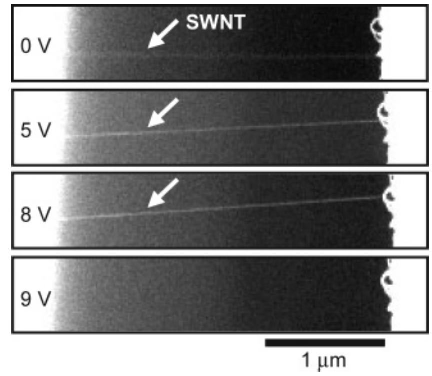

Figure 7. Example of SEM images under stretching. Indicated voltage is the applied V_{piezo}. Arrows indicate the suspended SWNT. The SWNT is disappeared at $V_{piezo} = 9$ V because the broken (or slipped off) SWNT is bended into the crack.

In conclusion, we have fabricated the new devices for applying uniaxial strain to the suspended SWNTs, and the form and the optical properties of the individual suspended SWNT under stretching are investigated. The processes of the deformation and the break of the SWNT under stretching were directly observed by SEM. In addition, from the PL measurement, the emission energy shift due to the band gap change is observed. The band gap change is caused by the elastic strain of the SWNT under stretching. Moreover, just before breaking, the emission intensity reduction due to the elastic strain of the SWNT is also observed. As stretching increases, various behaviors of the energy shifts are observed. These behaviors can be explained by the deformation processes observed by SEM. In this device, the strain is directly applied by the extension of piezoelectric device, therefore, it is expected to realize the fast modulation of the band gap. In addition, the unprocessed and uncovered SWNT is used in this device, therefore, the electrodes can be formed to the SWNT. Hence, this device is also expected to be applied to the tunable light-emitting devices.

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