In-situ TEM study on structural change and light emission of a multiwall carbon nanotube during Joule heating

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Abstract. Structure changes of a multiwall carbon nanotube (MWNT) during Joule heating were studied with simultaneous measurement of light emission spectra. The outer shells of the MWNT peeled off one by one because of excessive heating. All the peeled outer shells finally disappeared and inner shells whose tips were closed emerged, i.e., a new MWNT was formed. Each diameter of the shells comprising the MWNT decreased compared with those before the fracture. Light emission spectra during Joule heating of an MWNT were composed of both the blackbody radiation and characteristic peaks. The peaks in the light emission spectra shifted to higher energies in accordance with shrinkage of the inner shells. The energies of the peaks in the spectra corresponded to energy gaps between van Hove singularities calculated from the diameters of the shells, indicating that the peaks in the spectra are attributed to the interband electron transition in the MWNT.

1. Introduction
Carbon nanotube (CNT) can be regarded as a quasi-one-dimensional nanomaterial and has semiconducting or metallic properties depending on its structure. Electroluminescence [1-5], photoluminescence [6, 7] and thermal emission [8, 9] of CNTs have been reported. For thermal emission of multiwall carbon nanotubes (MWNTs), some broad emission peaks induced by electric current in addition to the blackbody radiation spectrum were observed in a scanning electron microscope (SEM) [10] and a scanning tunnelling microscope (STM) [11]. The emission peaks were interpreted to be derived from electronic transitions between van Hove singularities of the outermost shell of the MWNT. However, the contribution of each inner shell constituting an MWNT to the light emission has not been made clear yet. This is because SEM does not have spatial resolution enough to evaluate detailed structures of an MWNT, and STM cannot observe inner structures of an MWNT. In the present study, the inner structure changes of an MWNT during Joule heating were investigated by transmission electron microscopy (TEM) with simultaneous measurement of the light emission spectra.

2. Experimental
MWNTs were produced by the arc discharge method. MWNTs were attached to a knife edge of a gold (Au) plate by dielectrophoresis of an MWNT suspended in isopropanol. The Au plate was mounted on a movable stage in a specimen holder for TEM (JEM-2010, JEOL). In the microscope, a tip of an individual MWNT protruding from the Au plate (cathode) was brought into contact with an Au-coated tungsten needle which was fixed on a non-movable stage in the specimen holder and used as a counter
electrode (anode). Structure changes during Joule heating of the MWNT were observed using a television system. The acceleration voltage of TEM was 120 kV. TEM images, bias voltage, electric current, and light emitted from the MWNT were simultaneously recorded using a home-made in-situ observation system. Schematic of the experimental setup of the system is shown in figure 1.

3. Results and discussion
Figure 2 shows TEM images of structure changes in an MWNT during Joule heating. Peeling of the outer shells one by one was observed. Changes of electric conductance are shown in figure 3a. Step-like drops of the conductance were caused by peeling of the outer shells. While peeling the outer shells, conductance did not drop to zero, suggesting that electric current passed through inner shells of the MWNT. The light emission spectra observed simultaneously with the TEM images are shown in figure 3b. Light emission peaks were observed besides blackbody radiation spectra. With the peeling of the outermost shells, the intensity of the spectra and current decreased at the same time, but the peak positions did not change. After the peeling of the outermost shells, the second outer shell peeled off as well. Repeating this process caused the complete fracture of the body of the MWNT. After the fracture of the body of the MWNT, the tips of inner shells maintained closed shell structures. In other words, a new MWNT was formed, as shown in figure 4. This new MWNT is named the second MWNT. After the fracture of an $n$-th MWNT, the remaining MWNT is named $(n+1)$-th MWNT hereafter.

Figure 2. Peeling process of outer shells of an MWNT.
Figure 3. a) Changes in electric conductance of the MWNT shown in figure 2. Step-like drops of the conductance are caused by peeling of the outer shells. b) Spectra of light emission from the MWNT.

Figure 4. TEM images of 1st, 5th and 6th MWNTs. Shrinkage of the diameter of all shells and decrease of the number of shells composing the MWNT are observed.

TEM images of the 1st, 5th and 6th MWNT are shown in figures 4a, 4b and 4c respectively. The number of the shells in the 1st MWNT was 14. The number of the shells in the 5th MWNT and the 6th MWNT decreased from 14 to 11 and 7, respectively. In addition, the diameters of all shells of the formed MWNT were found to have decreased; the amount of shrinkage for all shells was about 0.4 - 0.7 nm. Figure 5 shows light emission spectra from the 1st, 5th and 6th MWNTs during Joule heating at a constant electric power of 390 µW (2.5 V and 155 µA). In these spectra, some emission peaks were observed. Changes of the peaks with the structure changes of the MWNT are as follows; i) the intensity of the peaks increases, ii) the shape of the peaks becomes sharp, and iii) the peaks slightly shift to higher energy. The peaks in the light emission spectra from the 6th MWNT appear at 550, 590, 677, 729, 771, 790, 815 and 890 nm. In the previous study on light emission from a MWNT using STM, it was suggested that the photon energies corresponded to energy gaps between van Hove singularities in electric density of state of the outermost shell [11]. In the present study, however, photon energies from the 6th MWNT did not completely correspond to estimated energy gaps even if the outermost shell was regarded as either a semiconducting or a metallic shell. Then, the energy gaps were calculated from all the diameters including inner shells, as shown in table 1. The broad peak at around 590 nm in figure 5, for example, can be explained by 575, 585, 600, 606 and 616 nm in this table. Also, the breakdown of
outer shells was observed during Joule heating. So, the temperature of the MWNT was expected to be higher than 2,200 K [10]. In this situation, not only semiconducting shells of the MWNT but also metallic ones may contribute to the light emission because electrons in the CNT are thermally excited into van Hove singularities above the Fermi level and lead to the recombination with created holes, resulting in the emission of photons.

**Figure 5.** Light emission spectra at a constant electrical power (390 µW). The peak positions shifted to higher energy due to the shrinkage of tube diameters after the fracture.

**Table 1.** Expected peak wavelengths calculated from diameters of inner shells of the 6th MWNT. a) In case that each shell is semiconducting. b) In case that each shell is metallic.

| SHELL No. | 1   | 2   | 3   | 4   | 5   | 6   | 7   |
|-----------|-----|-----|-----|-----|-----|-----|-----|
| diameter (nm) | 2.17 | 2.91 | 3.62 | 4.43 | 5.05 | 5.73 | 6.38 |
| E11   | 816  | 1096 | 1364 | 1667 | 1900 | 2157 | 2401 |
| E33   | 652  | 877  | 1091 | 1334 | 1520 | 1726 | 1921 |
| E44   | 466  | 626  | 779  | 953  | 1086 | 1233 | 1372 |
| E55   | 408  | 548  | 682  | 834  | 950  | 1078 | 1201 |
| E66   | 326  | 438  | 545  | 667  | 760  | 863  | 961  |
| E77   | 399  | 496  | 606  | 691  | 784  | 873  |       |
| E88   | 420  | 513  | 585  | 664  | 739  |       |       |
| E99   | 390  | 476  | 543  | 616  | 686  |       |       |

**Table 1 (b)**

| SHELL No. | 1   | 2   | 3   | 4   | 5   | 6   | 7   |
|-----------|-----|-----|-----|-----|-----|-----|-----|
| diameter (nm) | 2.17 | 2.91 | 3.62 | 4.43 | 5.05 | 5.73 | 6.38 |
| E22   | 544  | 731  | 909  | 1111 | 1267 | 1438 | 1601 |
| E33   | 362  | 487  | 606  | 741  | 844  | 959  | 1067 |
| E44   | 365  | 455  | 556  | 633  | 719  | 800  |       |
| E55   | 364  | 445  | 507  | 575  | 640  |       |       |
| E66   | 370  | 422  | 479  | 534  |       |       |       |
| E77   | 362  | 411  | 457  |       |       |       |       |
| E88   | 359  | 400  |       |       |       |       |       |
| E99   | 356  |       |       |       |       |       |       |

The aforementioned changes of the emission peaks in the spectra (figure 5) can be explained as follows: reduction of the diameter of the shells brings about the widening of the energy gaps between van Hove singularities, and causes the shift of the peak positions to higher energy. In the new MWNT (after the fracture), the number of the shells which contributes to light emission decreased as compared with the old MWNT (before the fracture). So, the peaks in the spectra related with inner shells after the fracture are expected to be more distinctive than those before the fracture.
Since the inner shells contribute to current flow, as revealed in figure 3a, the inner shells are heated to high temperatures due to Joule heating to excite electrons thermally to high energy levels. The present observation shows that not only outer shells but also inner shells contribute to the light emission from an MWNT through the interband transitions of thermally excited electrons.

4. Conclusion
We investigated the structure changes and light emission mechanism of an MWNT during Joule heating by in-situ TEM. Peeling of the outer shells of the MWNT and fracture of its body were observed. In the light emission spectra, some peaks besides blackbody radiation were observed. After the structure changes of the MWNT, the decrease of the peak intensity and the shifts of the peaks were observed, which are due to the reduction of the diameter of shells contributing the light emission. The wavelengths of the light emission peaks could be explained by energy gaps between van Hove singularities of the MWNT. The present results showed that the light emission from an MWNT during Joule heating contains interband transitions in inner shells of the MWNT as well as outer shells.

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