Formation of Azafullerene Encapsulated Single-Walled Carbon Nanotubes Using Plasma Ion Irradiation Method

Yohei HANABUSA, Toshiro KANEKO, and Rikizo HATAKEYAMA
Department of Electronic Engineering, Tohoku University, Aoba 6-6-05, Aoba-ku, Sendai 980-8579, Japan

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The synthesis of azafullerene $C_{59}N$ is realized through a nitrogen plasma irradiation method, which is confirmed by the analysis of mass spectroscopy. A plasma consisting of a fullerene negative ion C_{60}^- and the azafullerene positive ion $C_{59}N^+$ (C_{60}^--$C_{59}N^+$ plasma) is generated by means of an electron beam ionization. C_{60}^- and $C_{59}N^+$ ions are selectively irradiated to single-walled carbon nanotubes (SWNTs) put on a substrate which is positively or negatively biased, respectively. The electrical transport properties of C_{60}^- and $C_{59}N^+$ irradiated SWNTs are investigated by fabricating them as the channels of field-effect transistor devices in vacuum at room temperature. C_{60}^- irradiated SWNTs realized by the positive substrate bias show the p-type transport property. On the other hand, $C_{59}N^+$ irradiated SWNTs realized by the negative substrate bias exhibit the n-type characteristic.

Keywords: plasma ion irradiation, electron beam ionization, fullerene, carbon nanotubes, field effect transistor

1. Introduction

Single-walled carbon nanotubes (SWNTs) have a significant potential in creating novel nano electronic devices by encapsulating molecules or atoms inside their hollow space. Up to now, we have developed SWNT-based field effect transistors (FETs), where alkali-metal positive ions or fullerene negative ions are encapsulated into the SWNTs using a plasma irradiation method [1-3]. Since it is theoretically reported that the fullerene C_{60} and an azafullerene $C_{59}N$ can work as an electron acceptor and donor [4], respectively, the encapsulated fullerenes are expected to realize the ideal one-dimensional p-n junction in the SWNTs. The encapsulation of C_{60} and $C_{59}N$ into the SWNTs has been realized via a vapor diffusion method, and the electrical transport property of the C_{60} encapsulated SWNT (C_{60}@SWNT) exhibits an enhanced p-type characteristic compared with that of the pristine SWNT, whereas the $C_{59}N$@SWNT shows an n-type behavior [5]. However, selective insertion of C_{60} and $C_{59}N$ in one SWNT is difficult in this case. Therefore, in this study, we use C_{60} and $C_{59}N$ as negative (C_{60}^-) and positive ($C_{59}N^+$) ions, and attempt to encapsulate them separately into the SWNT using the plasma ion irradiation method.

2. Experimental Apparatus

The azafullerene $C_{59}N$ is synthesized using a plasma

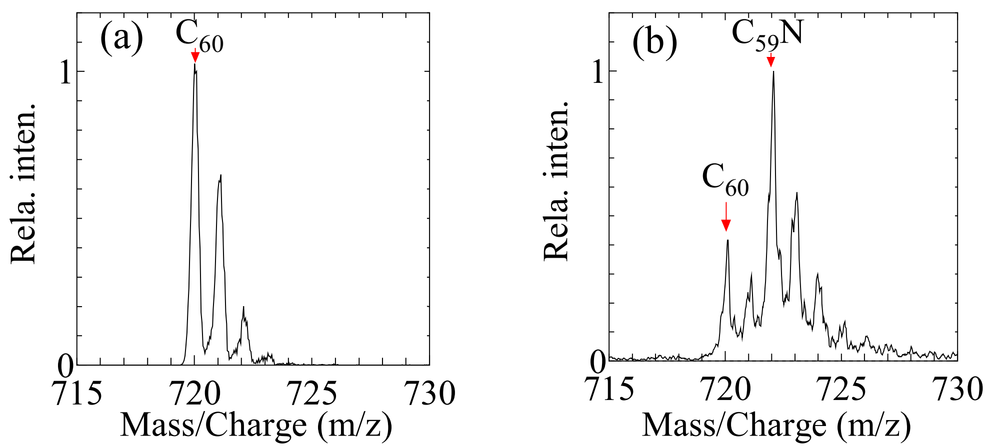

Fig. 1 Mass spectra of (a) a solution and (b) a residue in plasma-irradiated fullerene dissolved toluene in a positive ion mode of LD-TOF-MS.

author's e-mail:hanabusa@plasma.icie.tohoku.ac.jp

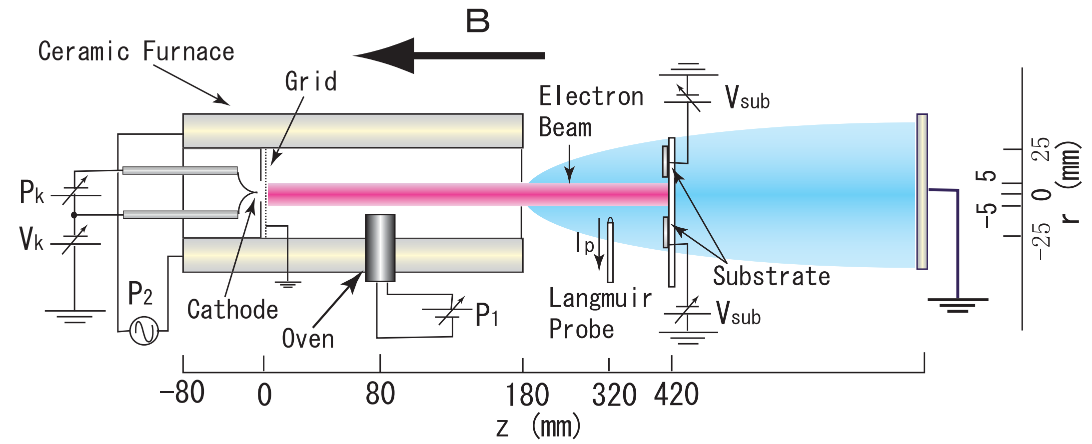

Fig. 2 Schematic of an experimental apparatus.

irradiation method [6]. The fullerene C_{60} after nitrogen plasma irradiation is dissolved in toluene, and its mixture is separated into a residue and a solution. The mass spectroscopy analysis of the formed azafullerene is performed using a laser-desorption time-of-flight mass spectrometer (LD-TOF-MS, Shimadzu AXIMA-CFR+). Figure 1 shows mass spectra of (a) the solution and (b) the residue in plasma-irradiated fullerene dissolved toluene in a positive ion mode of the LD-TOD-MS. The peak at the mass number 722 is the most distinct in the residue [Fig. 1(b)], which mainly originates from $C_{59}N$. Although, the mass number 722 is the sum of mass peaks of $C_{59}N$ and $^{12}C_{58}{}^{13}C_2$, $^{12}C_{58}{}^{13}C_2$ is less than 10 % of $^{12}C_{60}$, and then, $C_{59}N$ is dominant in this peak. In the solution, however, the peak intensity corresponding to $C_{59}N$ is not observed [Fig. 1(a)]. Because $C_{59}N$ molecules dissolve little in toluene, it is dominant in the residue, while the quantitative abundance ratio of $C_{59}N$ to C_{60} is not determined from the results of LD-TOF-MS.

The C_{60}^--$C_{59}N^+$ plasma is generated by means of an electron beam ionization [7]. The plasma source setup in a vacuum chamber is schematically shown in Fig. 2. Thermionic electrons are emitted from a tungsten cathode by applying the DC power P_k, and are accelerated by a potential difference between the cathode V_k and a grounded grid located at z = 0 mm. The C_{60} and $C_{59}N$ mixture loaded in an oven is sublimated by heating. C_{60} molecules attract low temperature electrons, while $C_{59}N$ molecules are ionized by the electron beam. The C_{60}^--$C_{59}N^+$ plasma is generated radially outside of the electron beam by a magnetic filter effect. SWNTs prepared by an arc-discharge method are put on a stainless steel substrate (15 mm × 15 mm) located at z = 420 mm and r = ±5 mm. C_{60}^- and $C_{59}N^+$ ions are irradiated to SWNTs by applying substrate biases of V_{sub} = +20 V and −20 V, respectively. The ion irradiating time, magnetic field, cathode bias voltage, and background gas pressure are t = 1 h, B = 3 kG, V_k = −20 V, and $P = 1 \times 10^{-3}$ Pa, respectively.

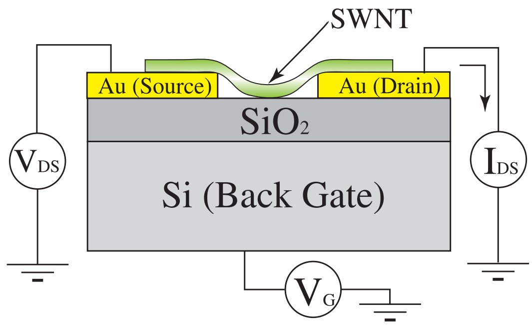

Fig. 3 Schematic of the SWNT-based FET device.

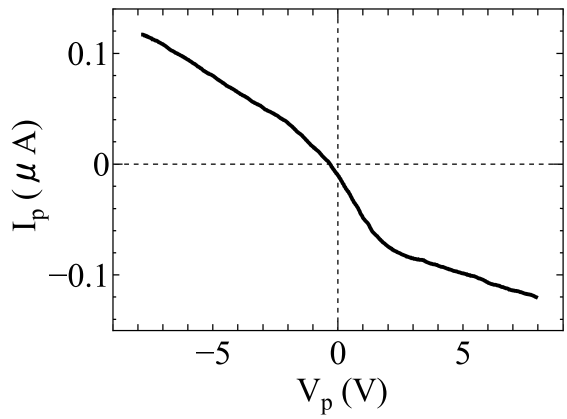

Fig. 4 Langmuir-probe characteristic of C_{60}^--$C_{59}N^+$ plasma at z = 320 mm and r = −5 mm under B = 3 kG.

The electrical transport properties of C_{60}^- and $C_{59}N^+$ irradiated SWNTs are investigated by fabricating them as the channels of FET devices in vacuum at room temperature. The FET device is schematically shown in Fig. 3. The detailed fabrication process is given as follows. Pristine and plasma-ion irradiated SWNTs are suspended by sonication in N,N-dimethylformamide (DMF) solvent. After sonication, SWNTs are spincoated onto an FET substrate on which Au source and drain electrodes (distance between both electrodes is 500 nm) are formed. The substrates are baked at about 100 ℃ for 30 minutes to remove DMF solvent.

3. Experimental Results and Discussion

Figure 4 gives a typical Langumuir-probe characteristic of the generated C_{60}^{-}-$C_{59}N^{+}$ plasma at z = 320 mm and r = −5 mm. The saturation current ratio of the negative ions to the positive ions is almost unity, which indicates that the masses of positive and negative ions are nearly equal, i.e., there is almost no electron [7]. Figure 5 shows mass spectra of deposits on the substrate which is (a) positively and (b) negatively biased, where LD-TOF-MS is operated in the positive ion mode. A mass peak of C_{60} is measured from the deposit on the positively biased substrate. The deposit on the negatively biased substrate shows both the C_{60} and $C_{59}N$ peaks. This result indicates that the $C_{59}N^{+}$ ions are selectively irradiated to negatively biased substrate.

Figure 6 shows Raman spectra of the pristine, C_{60}^{-} ions irradiated, and $C_{59}N^{+}$ ions irradiated SWNTs in the range of (a) 100-400 cm^{-1} (radial breathing mode, RBM) and (b) 1200-1700 cm^{-1}. The Raman spectra are obtained at an excitation wavelength of 488 nm. The spectrum shapes of the C_{60}^{-} or $C_{59}N^{+}$ ions irradiated SWNTs drastically change in comparison with that of the pristine SWNTs, where an increase in the peak intensity at 197 cm^{-1} is observed. The results of Raman spectra in the RBM region give indirect evidence of the encapsulation of C_{60} or $C_{59}N$ inside SWNTs. In addition, the ratio of G band (1590 cm^{-1}) to D band (1350 cm^{-1}) has no change for encapsulated SWNTs compared with that of the pristine SWNTs. This result suggests that the plasma irradiation gives little damage on the structure of SWNTs.

The electrical transport property of the pristine semiconducting SWNT is known to exhibit the p-type

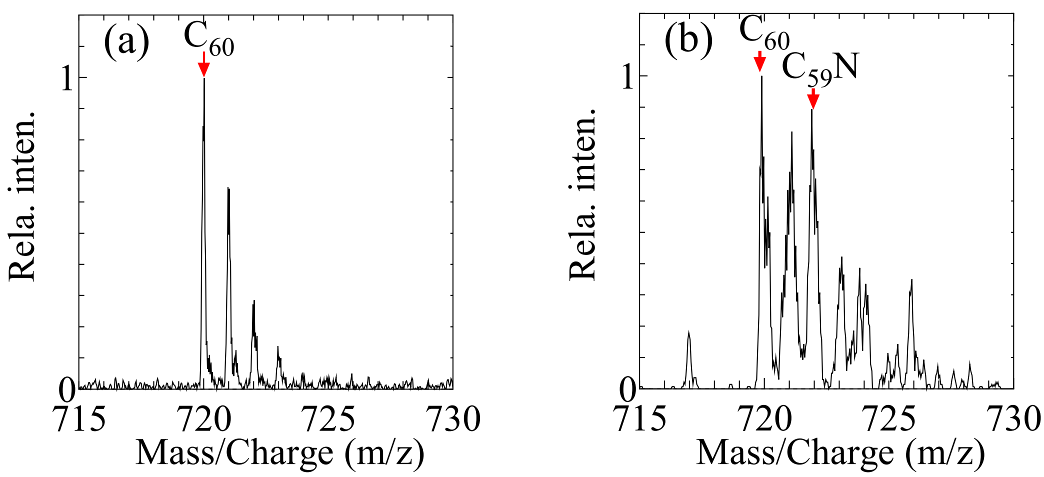

Fig. 5 Mass spectra of deposits on a substrate which is (a) positively and (b) negatively biased, where LD-TOF-MS is operated in the positive ion mode.

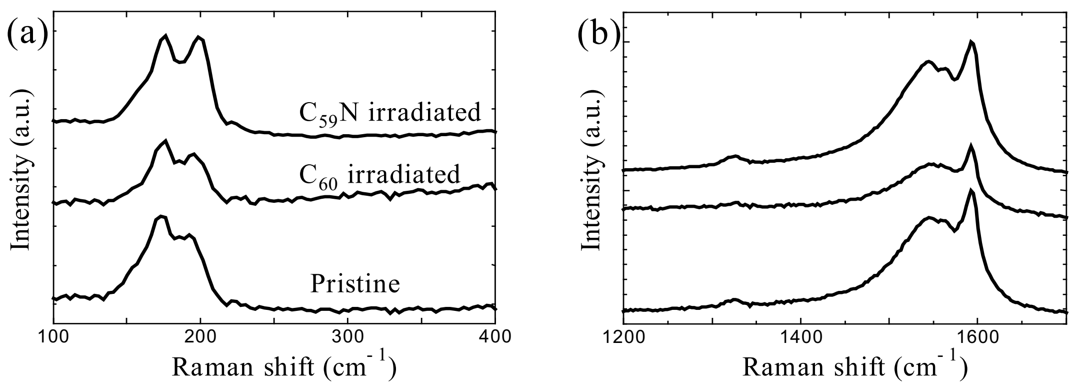

Fig. 6 Raman spectra for the pristine, C_{60} irradiated, and $C_{59}N$ irradiated SWNTs in the range of (a) 100-400 cm^{-1} (radial breathing mode) and (b) 1200-1700 cm^{-1}. The Raman spectra are obtained at an excitation wavelength of 488 nm.

behavior as shown in Fig. 7(a), where a curve of source-drain current I_{DS} vs. gate voltage V_G is described at a source-drain voltage V_{DS} = 1 V. Figure 7(b) displays the transport characteristic of the C_{60}^- ions irradiated SWNT prepared with V_{sub} = +20 V. The typical p-type characteristic is still observed, but the threshold gate voltage for hole conductance is found to show an upshift from −25 V to −10 V compared with that of the pristine SWNTs, indicating that the p-type behavior of the SWNTs is enhanced by the C_{60} encapsulation. In contrast, the transport property of the $C_{59}N^+$ ions irradiated SWNT prepared by applying V_{sub} = –20 V drastically changes to n-type semiconducting one, as shown in Fig. 7(c). This n-type characteristic is attributed to $C_{59}N$ encapsulation into the SWNT, suggesting that $C_{59}N$ exerts a strong electron donor effect on the SWNT.

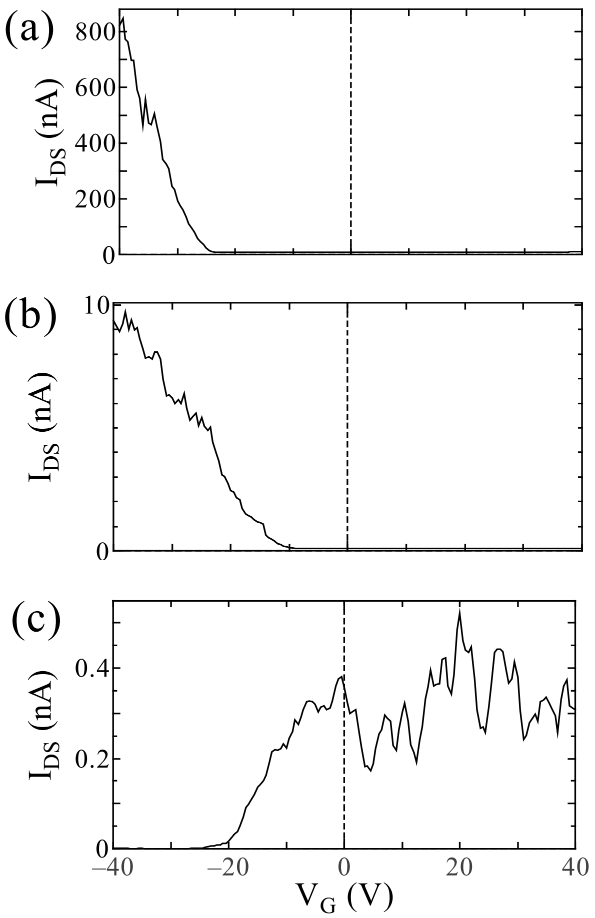

Fig. 7: Electrical transport characteristics [source-drain current (I_{DS}) - gate voltage (V_G)] measured with V_{DS} = 1 V at room temperature for (a) pristine SWNT, (b) C_{60} encapsulated, and (c) $C_{59}N$ encapsulated SWNTs.

4. Conclusions

The plasma consisting of C_{60}^- and $C_{59}N^+$ ions is generated through the electron beam ionization. C_{60}^- and $C_{59}N^+$ ions are selectively irradiated to the positively and negatively biased substrate, respectively. The Raman spectrum shape of the C_{60}^- or $C_{59}N^+$ irradiated SWNTs drastically changes in comparison with that of pristine SWNTs. C_{60}^- irradiated SWNTs realized by positive substrate biases show the p-type semiconducting transport property. On the contrary, $C_{59}N^+$ irradiated SWNTs realized by negative substrate biases exhibit the n-type characteristic.

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