Processing and Electric Property Control of Carbon Nanotubes by Low-energy Electron Irradiation

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Abstract

We have recently discovered that low-energy electron irradiation damages single-walled carbon nanotubes. This phenomenon can be exploited to achieve spatially selective removal of single-walled carbon nanotubes and control their electric properties over a wide range. The selective removal will make it possible to fabricate various nanotube architectures. The electric properties of metallic nanotubes can be converted to semiconducting, and further electron irradiation finally makes them insulating. It appears that these irradiation-induced changes in the electric properties are similar to those that would be expected if chirality were controlled.

1. Introduction

Single-walled carbon nanotubes (SWNTs) are promising for future nanoelectronics because of their quasi-one-dimensional structure and excellent electric properties. Carbon nanotubes can be semiconducting or metallic, depending on their chirality (the chirality determines the nanotube structure, such as the diameter and wrapping angle). A semiconducting SWNT can be used as a field effect transistor (FET) with high mobility [1]. On the other hand, a metallic SWNT can work as an interconnecting wire with high chemical stability and large current capability [2], [3].

However, some serious problems have prevented the fabrication of nanotube-based integrated circuits. First, there is no established way to place individual SWNTs precisely at desired positions. Although it is possible to control where SWNTs start to grow by patterning a catalytic metal layer by conventional lithography, it is still impossible to control the growth direction of individual SWNTs independently. Thus, high-density nanotube growth almost always results in the growth of unnecessary SWNTs at undesired positions, which could cause short circuits. Another problem is that it is still impossible to control the chirality of SWNTs as they grow. Thus, synthesized SWNT samples contain both metallic and semiconducting types. A metallic SWNT does not work as a FET. The bandgap of semiconducting SWNTs varies widely, which causes irregularities in the FET performance.

Due to the high chemical stability of graphene sheets, it had been generally assumed that electron irradiation does not cause any structural damage to SWNTs when the electron energy is below the threshold energy (86 keV [4]) for knock-on damage. However, our recent study clearly showed that low-energy (500 eV to 25 keV) electron irradiation causes severe damage to SWNTs [5]. In this paper, we show that we can exploit this low-energy electron irradiation damage to selectively remove unnecessary SWNTs at undesired positions [6], [7] and convert the electric properties of metallic SWNTs to semiconducting [8] or insulating [9].

2. Experimental

SWNTs were grown on SiO2/Si substrates by the thermal chemical vapor deposition (CVD) method, using methane or ethanol as a carbon source and Co as a catalyst. SWNT-FETs were fabricated by depositing Ti/Au electrodes on the SWNTs using conventional lithography and lift-off techniques. The substrate (heavily doped p-type Si with 100-nm-thick thermally oxidized SiO_2) worked as a back gate.

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Electron irradiation was performed at room temperature in a Hitachi S-4300 cold cathode field-emission scanning electron microscope (SEM). Four microprobes were installed in the SEM for *in-situ* electric measurements during electron irradiation. Each microprobe can be actuated by piezo-devices independently. Micro Raman spectra were obtained in air at the excitation laser wavelength of 785 nm.

3. Spatially selective removal of SWNTs

The procedure for the spatially selective removal of SWNTs is schematically shown in **Fig. 1** [6], [7]. In this study, suspended SWNTs were grown on a patterned substrate because that makes them easy to observe by SEM. The acceleration voltage of the electrons was 1 kV, which causes severe damage [5]. As shown in the figure, part of the SWNT sample was irradiated by the electron beam for five minutes using the line-scan mode. The scanned line length was about 125 μm and the beam current was about 50 pA. Assuming that the spot size of the electron beam was 5 nm, we estimated that the irradiation dose was 1.5 $\times$ 10^{19} cm^{-2}. The irradiated positions of the SWNTs were severely damaged by low-energy electron irradiation damage. Raman spectra of the irradiated SWNTs were measured to identify the irradiation damage [5]. **Figure 2** shows (a) tangential mode (G) and disorder-derived (D) bands and (b) the radial breathing mode (RBM) region of the Raman spectra of SWNTs before and after electron irradiation. The SWNTs were irradiated by 1-keV electrons up to a dose of 8 $\times$ 10^{17} cm^{-2} in the normal observation mode. The irradiation significantly decreased the G-band intensity and this resulted in a drastic decrease in the G/D ratio, which is often used as an indicator of the crystallinity of SWNTs. The RBM peaks almost vanished after the irradiation, as shown in Fig. 2(b), indicating that the characteristic optical properties of the SWNTs disappeared because of the irradiation damage. Note that the irradiation dose given by the line scan was much larger than the dose in this case, so the local damage caused by the line scan would be much severer than that shown in Fig. 2. We think that the damage is due to the formation of dangling bonds caused by C-C bond breaking, which is stabilized by the strain energy release in the sidewall of a SWNT. A detailed discussion is given elsewhere [10]-[12].

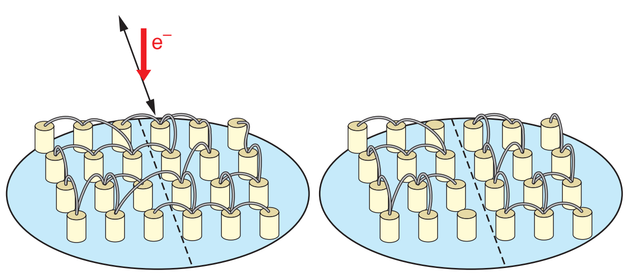

Fig. 1. Selective removal of SWNTs. (a) Some SWNTs are irradiated by the electron beam and damaged. (b) Damaged SWNTs are preferentially removed by annealing in air.

After the electron irradiation, the sample was annealed in air at 420°C for 30 min. The annealing preferentially eliminated the irradiated SWNTs, as shown in Fig. 1(b), because the damage reduced their robustness to annealing in air [5].

A SEM image of the sample after the procedure is

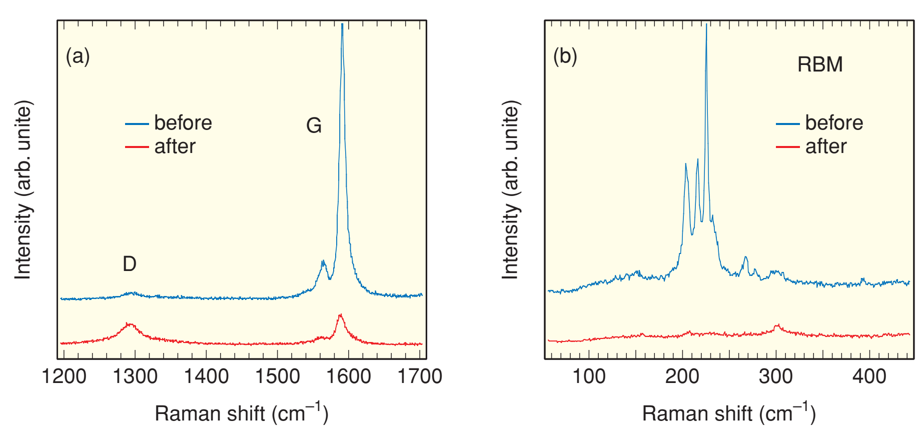

Fig. 2. Raman spectra of SWNTs before and after electron irradiation: (a) G- and D-bands and (b) RBM regions. In (b), the small humps at 300 cm^{-1} are from the substrate.

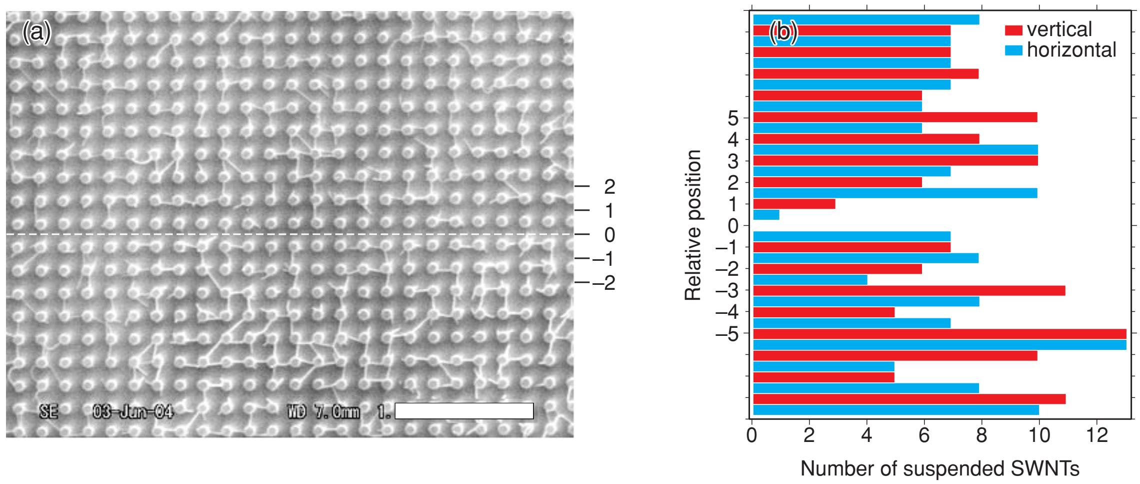

Fig. 3. (a) SEM image of the SWNT sample after the selective removal procedure. The irradiation line is denoted by the dashed line. Scale bar: 2.5 μm. (b) Position dependence of the number of SWNTs suspended between neighboring pillars.

shown in **Fig. 3(a)** [6], [7]. The dashed line indicates the line along which the electron beam was scanned. No SWNTs cross the line, although there are still many suspended SWNTs far from the line. This means that the irradiated i.e., damaged, SWNTs were selectively removed by the annealing in air. Using electron beam lithography, it should therefore be possible to fabricate various kinds of SWNT architectures by removing unnecessary SWNTs from a high-density SWNT network.

We estimated the spatial resolution of the selective removal procedure from Fig. 3(a). The position dependence of the number of remaining SWNTs suspended vertically and horizontally between the pillars is shown in **Fig. 3(b)** (diagonally suspended SWNTs were neglected). The relative positions are indicated in increments of the pillar pitch of 400 nm. The results show that the effects of the irradiation almost completely disappeared about 800 nm from the irradiation line. Such a high spatial resolution can be easily obtained because of the small spot size of the electron gun.

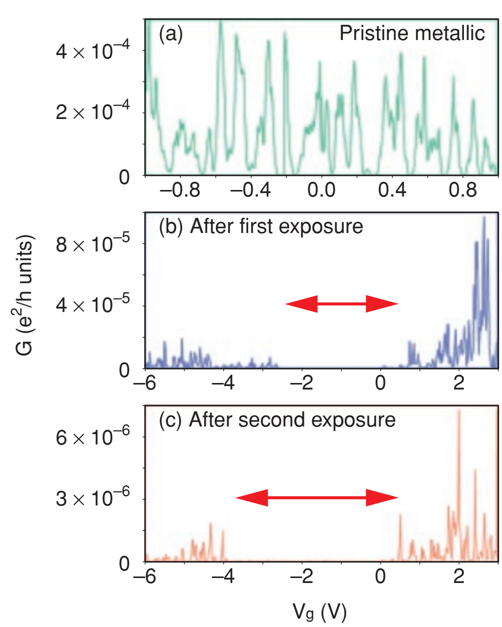

Fig. 4. Gate voltage characteristics of an initially metallic SWNT device: (a) before irradiation, (b) after the first irradiation, and (c) after the second irradiation.

4. Electric property changes induced by electron irradiation

4.1 Metal-semiconductor transition

The electric properties are much more sensitively changed by low-energy electron irradiation than the Raman spectra are. The initial gate voltage characteristics of a SWNT-FET device measured at 28 K are shown in **Fig. 4(a)** [8]. The gate-dependent oscillation of the conductance is due to single-electron transistor characteristics caused by a Coulomb blockade. Other than the Coulomb oscillation, the device showed no off-region in the whole gate voltage range, indicating that the SWNT was metallic. The device was exposed to an electron beam of 1 keV up to a dose of about 10^{15} cm^{-2}. Despite the very small dose, the gate voltage characteristics after the irradiation changed considerably, as shown in **Fig. 4(b)**: an off-region distinctly appeared around the gate voltage of 0 V, although the conductance peaks still existed on both the negative and positive gate voltage sides. The appearance of the off-region is a characteristic of semiconducting SWNTs. These results indicate that the electric properties of the SWNT device were converted from metallic to ambipolar semiconducting simply by the low-energy electron irradiation. Further irradiation resulted in an increase of the off-region, as shown in **Fig. 4(c)**. In general, the width of the off-region reflects the bandgap of SWNTs. The device characteristics changed as if second irradiation had caused an increase in the bandgap. In appearance, the irradiation-induced bandgap would be tunable. What is important here is that the metal-semiconductor transition and the extension of the off-region caused by the low-energy electron irradiation are phenomena that would be expected if the chirality of the SWNT were changed.

Here, we discuss a possible mechanism for the metal-semiconductor transition [13]. The temperature dependence of the device characteristics after the second irradiation is shown in **Fig. 5** [8]. The off-region in the gate voltage characteristics was distinctly observed below 60 K, but not at room temperature (295 K). This means that electrons encountered an energy barrier that they could overcome at room temperature, but not at low temperatures. From an Arrhenius plot of the conductivity at around a gate voltage of 0 V (off-region), the typical barrier height was determined to be 50-60 meV. It has been shown that a defect acts as a transport barrier in SWNT-FETs regardless of the defect formation method, such as ion irradiation [14], chemical processing [15], or atomic force microscopy (AFM) manipulation [16]. The origin of the energy barrier in our case seems to be defects caused by low-energy electron irradiation. The device characteristics in the off-region in Fig. 5 can be explained by the barrier formation. The nominal bandgap increases because the barrier height increases with increasing irradiation dose. The next question [13] is: why does the device turn on at larger gate voltages? We think this is due to gate-voltage-induced band bending (dE) in metallic SWNTs. The gate-induced charge (Q) is calculated by $Q = C{\cdot}V_G$, where C is the gate capacitance and V_G is the gate voltage. C is given by $C = 2\pi\varepsilon\varepsilon_o/ln(2h/r)$, where ε is the relative dielectric constant of gate insulator material, ε_o is the dielectric constant of vacuum, h is the thickness of the gate insulator, and r is the radius of the SWNT channel. The gate-induced electrons (holes) occupy the unoccupied (occupied) electronic states of the SWNT. The density of states near the Fermi level of a metallic SWNT is very low (0.02 to 0.04 states/eV/atom), and this results in a considerable amount of band bending. The estimated value of dE per V_G approaches 40 to 50 meV. Due to the band bending, the effective barrier height is reduced, as schematically shown in **Fig. 6**. The typical height of

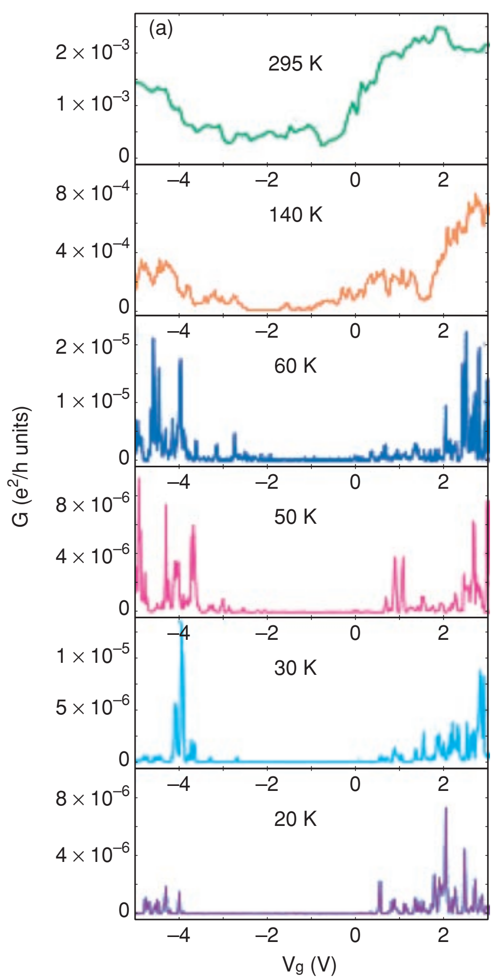

Fig. 5. Gate voltage characteristics of the SWNT device obtained at various temperatures after the second irradiation.

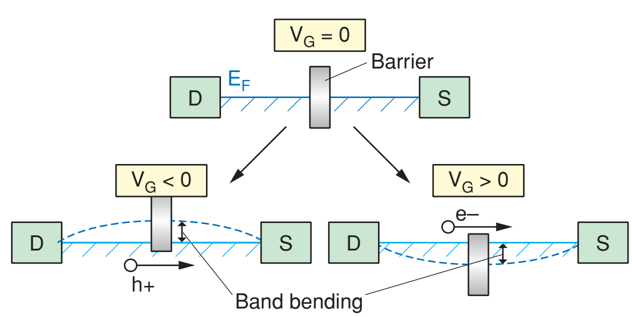

Fig. 6. Schematic model of the mechanism for the metal-to-semiconductor transition induced by low-energy electron irradiation.

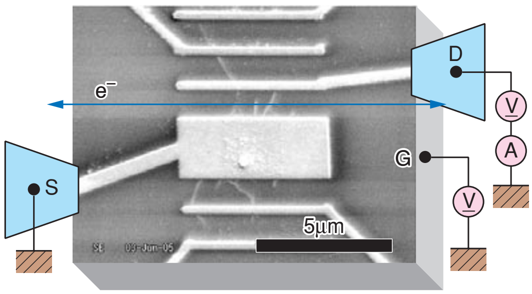

Fig. 7. SEM image of a device and a schematic of *in-situ* electrical measurements during electron irradiation. Neighboring electrodes were used as drain (D) and source (S) electrodes.

the barrier formed by the irradiation-induced defects is 50 to 60 meV, as mentioned above. Thus, at a gate voltage of several volts, the carriers could go through the channel without being blocked by the barrier.

4.2 Making SWNTs insulating

The effects of intensive electron irradiation were measured by *in-situ* electric measurements during electron irradiation in the SEM [9]. A typical SWNT-FET structure and a schematic of the measurement are shown in **Fig. 7**. Two microprobes were attached to pads connected to the drain and source electrodes. Then, the device was exposed to an electron beam while the drain-source current (I_D) was monitored at a constant drain-source voltage (V_D) and V_G. In this case, electron kinetic energy was set to 20 keV.

The dependence of the drain-source current (I_D) of a metallic SWNT device on irradiation time is shown in **Fig. 8**. The drain and back-gate voltages were 0.1 and 0 V, respectively. The entire device was first irradiated while the SEM was in the normal observation mode. The irradiated area was about 26 × 16 µm^2 (magnification of 5000), and the beam current was 290 pA. The resulting dose was estimated to be about 3.7×10^{14} cm^{-2}·s^{-1}. The current drastically decreased just after the irradiation started. Note that the electron energy of 20 keV used in this measurement is much less destructive than lower energies, such as 1 keV [5]. At 10 s, part of the SWNT was intensively irradiated using the line scan mode. The dose rate was estimated to be about 1.4×10^{18} cm^{-2}·s^{-1}. The current rapidly decreased and stayed almost constant at 10^{-11} A. After the line scan was stopped at 140 s, current of only 10^{-12} A was observed. That is, the two-probe conductivity (I_D/V_D) decreased by about six orders of magnitude from that of the initial state. A similar conductivity decrease was also observed for a semi-

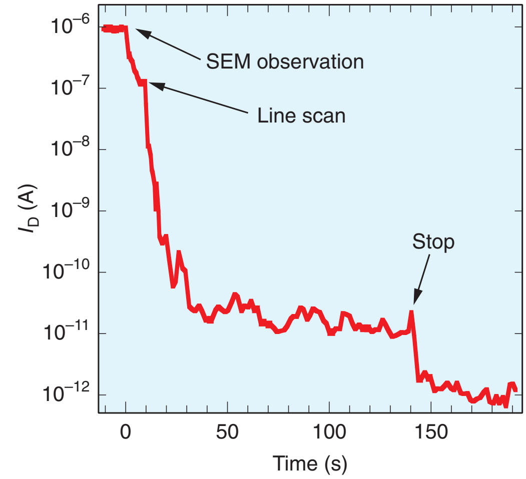

Fig. 8. Time evolution of I_D of a metallic SWNT device during electron irradiation.

conducting SWNT in the on state [9]. These results indicate that intensive electron irradiation makes metallic and semiconducting SWNTs almost insulating.

5. Conclusions

Low-energy electron irradiation damage can be used to remove unnecessary SWNTs with high spatial resolution to control the electric properties of SWNTs. The spatially selective removal of SWNTs from a high density random SWNT network will make it possible to fabricate various SWNT architectures. The electric properties of SWNTs can be controlled over a wide range, from metallic through semiconducting to almost insulating, simply by electron irradiation. The irradiation effects on the electric properties are similar to those expected if the chirality of a SWNT were controlled.

Acknowledgments

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