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Control of Electrical Properties of Single-walled Carbon Nanotubes by Low-energy Electron Irradiation

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1. Introduction

A carbon nanotube (CNT) is a molecular-scale wire that can be used as channel of field effect transistors (FET) owing to its intriguing transport properties. CNTs act as metal or semiconductor, depending on their chirality [1]. The chirality, however, cannot be controlled by the CNT synthesis method. Hence, FETs using as-grown single-walled carbon nanotubes (SWNTs) contain both metallic and semiconducting SWNTs. A metallic SWNT is insensitive to gate voltage so that it is generally useless as a channel. Field-selective devices using p-type, n-type or ambipolar semiconducting SWNTs will be useful for functional SWNT-FET fabrication.

We have focused on the low-energy electron beam irradiation as a way to modify the properties of SWNTs. Recently, our optical observations have shown that even low-energy electrons (100 eV – 25 keV) surely damage CNTs [2, 3], although the threshold energy of knock-on damage (86 keV) caused by the electron beam (EB) is known to be much higher [4]. Furthermore, we have reported EB-induced transition from metal to semiconductor at low temperature using SWNT-FETs [5]. In appearance, this EB-induced behavior of the SWNT-FETs seems to reveal similar electrical effects of the chirality change and the diameter change of SWNT, but the reason was not clear.

In this work, we studied the mechanism of the metal-semiconductor transition behavior of SWNT-FETs. The behavior is considered to arise from some defect induced by low-energy electron beam irradiation.

2. Experimental

Si substrate with 500 nm of surface SiO_2 was used as a starting material. SWNTs were synthesized on the substrate at low density by the CVD method using Co catalyst. Metal electrodes of Ti/Au were fabricated using a photolithography process and the lift-off method, resulting in metal-on-tube SWNT-FET that uses the substrate as a gate. EB irradiation was performed in vacuo with a scanning electron microscope (SEM). The acceleration voltage was 1 kV and beam current was 20 pA. The electronic properties of the SWNT-FET were observed at temperatures ranging from room temperature to 40 K.

3. Results and Discussion

Figure 1 shows drain current (I_D) vs. gate voltage (V_G) characteristics at 40 K before and after irradiation. Coulomb oscillation appeared due to a coulomb blockade at low temperature. Before irradiation, the SWNT-FET showed metallic characteristics originally [Fig. 1(a)]. When it was irradiated by the low-energy electron beam (1 keV, 2.8×10^{-6}C/cm^2), an off region (gap) opened up, that is, the I_D-V_G characteristics became semiconductive, i.e., sensitive to gate voltage [Fig. 1(b)].

To understand this metal-semiconductor transition, we first examined charging effect created by electron beam exposure because, in MOSFETs, threshold voltage (V_{TH}) change is generally related to FET charging. Charging effects on the V_{TH} mainly arise from fixed charges in the gate insulator and interface-trapped charges between the SWNT channel and gate insulator. If low-energy electron beam generates an appreciable fixed charge in the gate insulator, V_{TH} should be changed according to the dose. However, the apparent relation between V_{TH} and exposure dose was not observed (Fig. 2). The interface trap effect, determined by the change of subthreshold voltage swing with dose, did not show apparent relation, either. So, the charging effect generated by the exposure condition in this study would be negligible. In addition, it seems hard to explain the opening of the gap by the charging effect only.

Next, we examined the effect of EB irradiation on the SWNT channel itself. From Raman spectroscopy, it has been found that relatively high-dose EB exposure reduced chemical tolerance and made SWNT defective [3, 4]. In this study, even when EB dose was lowered further, the ratio of Raman signal of the D-band (disorder-induced feature) was increased by the EB irradiation (Fig. 3). In addition, the conductivity of the SWNT channel decreased with increasing dose (Fig. 4). These results indicate that the low-dose EB irradiation created some defects in the SWNT channel.

As shown in Fig. 5, the transition from metallic to semiconductive behavior by EB exposure was evident only at low temperature, not at room temperature. At room temperature, the originally metallic SWNT-FET maintained metallic characteristics even after EB irradiation. A complete structural change, such as a chirality change, would not seem to have occurred. The electrical modulation of the SWNT-FET is considered to be due to energetic barrier creation by some defect induced by low-energy EB irradiation. From Fig. 5, the created-barrier height can be passed over at room temperature.

4. Conclusions

Metallic SWNT-FETs can be changed to

semiconductive at low temperature by low-energy EB irradiation, while metallic characteristics were maintained at room temperature. This EB-induced metal-semiconductor transition is considered to be due to energetic barrier creation by some defect in the SWNT channel, not due to the charging effect of the EB. Low-energy EB exposure is advantageous in terms of selective exposure, spatial resolution, and throughput, so that it can be used to selectively produce the SWNT-FETs with a semiconductor channel at desired locations. There is also the possibility of tuning device characteristics by adjusting the EB dose and temperature.

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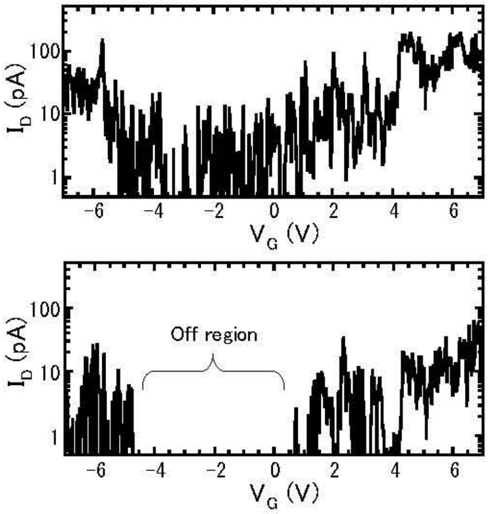

Figure 1. I_D-V_G characteristics before (a) and after (b) exposure at 40 K. The SWNT channel originally shows metallic characteristics. Drain voltage (V_D) is 5 mV. An off region was opened up by 1-keV EB irradiation (2.8x10^{-6} C/cm^2).

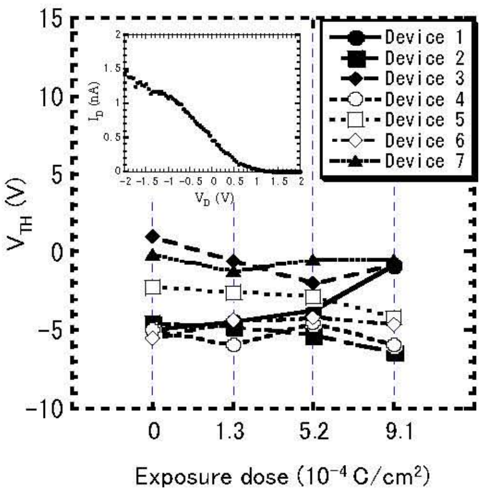

Figure 2. V_{TH} change of each device according to the exposure dose. V_{TH} was determined using the originally semiconducting SWNT-FET (p-type), whose typical characteristics are shown in the inset.

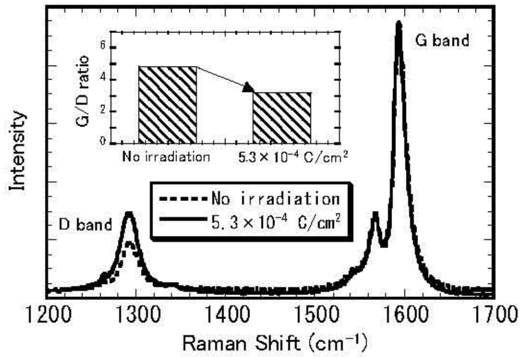

Figure 3. Raman spectra before and after irradiation. Suspended SWNTs on pillar patterns were used for this observation. The inset shows G/D ratio change before and after irradiation. The ratio decreased by low-energy EB irradiation (1 keV, 5.3 •~10^{-4} C/cm^2). The spectra were taken with a laser excitation of 785 nm.

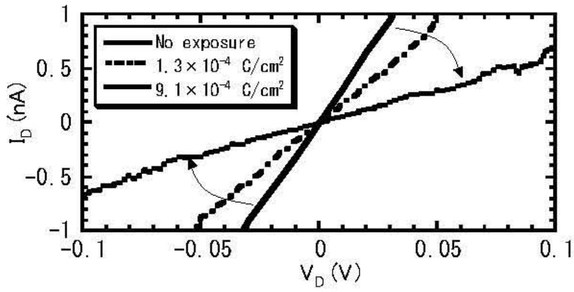

Figure 4. Changes in I_D-V_D characteristics with exposure dose observed at room temperature. Conductivity was decreased by EB irradiation.

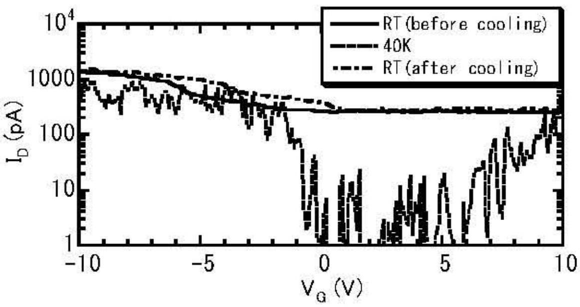

Figure 5. I_D-V_G characteristics after exposure at 9.1 •~10^{-4} C/cm^2 with temperature. V_D is 10 mV. I_D-V_G characteristics became semiconductive at 40 K, although they remained metallic before and after cooling.

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