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Optical Observation of Carrier Accumulation in Single-Walled Carbon Nanotube Transistors

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Electric-field-induced spectral changes in single-walled carbon nanotubes were studied using a thin-film transistor configuration. As a function of electric field, the optical spectra displayed continuous intensity modulations. This is the direct evidence of carrier accumulation, and the amount of accumulated carriers was quantitatively consistent with the carrier density in the nanoscale wire-form field-effect transistor model. [DOI: 10.1143/JJAP.45.L1190]

KEYWORDS: single-walled carbon nanotube, field-effect device, thin film, optical properties

A significant amount of basic research on single-walled carbon nanotubes (SWNTs) has sparked interest in the potential applications of these novel materials.1) One promising use of SWNTs is in field-effect transistors (FETs). Their mobilities can be as high as 100,000 $\mathrm{cm^2/(V{\cdot}s)}$,2) their current carrying capacity can exceed 10^9 $\mathrm{A/cm^2}$,3) and ON/OFF current ratios can be larger than 10^5.4) Recently, with palladium as the electrode material, Schottky barrier-free ballistic FETs have been realized, exhibiting high drive currents, excellent transconductance, and switching ratios of 10^6.5) These favorable intrinsic electrical characteristics make these single SWNT devices potentially attractive for a range of applications. However, even with the progress in device fabrication and performance of SWNT-FETs, the effect of gate voltage on SWNT materials has never been experimentally studied except in terms of transport properties. Very recently, Wu *et al.* reported the optical properties of electrolyte-gated SWNT thin films, and qualitatively observed the modulation of carrier density.6) The fabrication of back-gated thin-film transistors (TFTs) has also opened a way of applying spectroscopy to SWNT-FETs as a function of gate voltage7–9) and investigating the modified carrier density quantitatively.

Here, we report the electric-field-induced optical spectral changes of SWNT films using a TFT configuration. Under the gate electric field, the spectra of the SWNTs displayed continuous intensity modulation. These results provided evidence of carrier accumulation in SWNT-TFTs. The amount of accumulated carriers was quantitatively consistent with the carrier density in the nanoscale wire-form FET model. This is the first quantitatively observation of carrier density in SWNT-FETs.

A schematic of the device is drawn in Fig. 1(a). The device was fabricated as described in ref. 8. A heavily doped n-type silicon wafer, with a 400-nm-thick insulating SiO_2 layer, was used for the bottom electrode. Comb-shaped drain and source electrodes of 10/100-nm-thick Cr/Au, respectively, were fabricated on the surface of the SiO_2 layer. Finally, SWNTs were suspended in *N*,*N*-dimethylformamide and deposited. Here, SWNTs were synthesized by a laser ablation method, and then purified by a conventional method.10,11) To determine the film thickness of the SWNT-TFT, we prepared a thicker film and measured it using a profilometer. By normalizing with the absorption intensity ratio of the TFT and the thicker film, we then estimated the thickness of the TFT. The estimated thickness of the TFT was 25 nm. The transfer characteristic was measured using an Agilent Technology E5207 semiconductor parameter analyzer. Optical spectra were recorded on a commercial spectrometer (Nicolet MAGNA-IR 760) equipped with a globar lamp and a mercury cadmium telluride (MCT) detector.

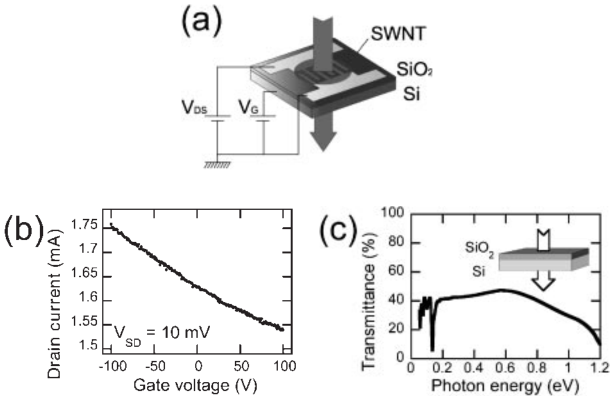

Fig. 1. (a) Schematic of TFT structure used in this study. The channel length and width of the devices were 30 μm and 38.8 mm, respectively. The arrow indicates the light path for optical probing. (b) Gate voltage dependence of source–drain current in a SWNT-TFT. (c) Optical absorption spectrum of a heavily doped n-type silicon wafer, with a 400-nm-thick insulating SiO_2 layer, which was used for SWNT-TFTs. Inset: Schematic of measurements.

Although we prepared a very thin SWNT film in previous study to reduce the contamination of metallic nanotubes,8,9) we used, in the present study, thick films to keep optical uniformity of films. Figure 1(b) shows the device characteristics of SWNT-TFTs, which was used in this study. Measurements of source–drain current versus gate bias voltage (V_G) were almost liner. The application of negative (positive) V_G increased (decreased) source–drain current, indicating that the transistor operates in the hole accumulation mode. No off-states were observed even at a positive V_G, indicating considerable contamination by the metallic SWNTs. Optical measurements of SWNT-TFTs were performed using the geometry shown in Fig. 1(a). The arrow in Fig. 1(a) indicates the light path for optical probing. Optical absorption spectrum of a heavily doped n-type silicon wafer,

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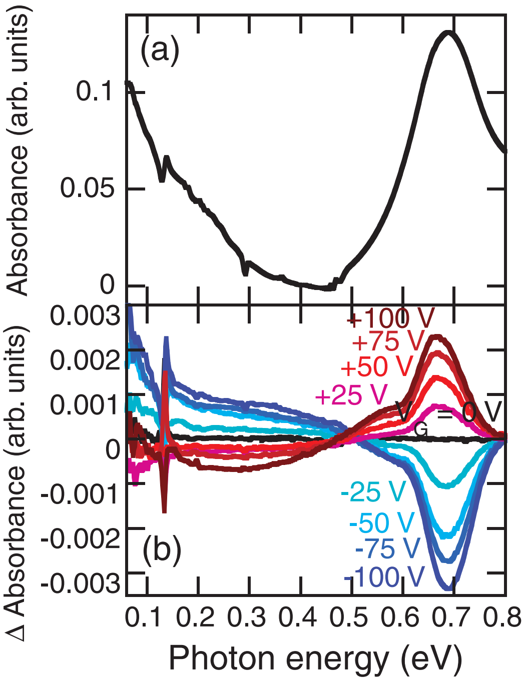

Fig. 2. (a) IR absorption spectrum of laser-SWNT-TFT. (b) Difference spectra (ΔA) between before and after gate bias (V_G) application. Data sets are displayed for every 25 V from $V_G = -100$ to 100 V.

with a 400-nm-thick insulating SiO_2 layer, was shown in Fig. 1(c). This substrate is sufficiently transparent for optical light from 0.1 to 1.1 eV, although a strong phonon absorption peak of SiO_2 exists at around 0.135 eV.

Figure 2(a) shows an IR absorption spectrum of a SWNT-TFT. The spectrum of the SWNT film was essentially identical to that already reported.[12,13] The broad peaks at approximately 0.68 eV correspond to the transitions between the two van Hove singularities in each semiconducting nanotube. In addition, a Drude-like absorption that is attribute to free carriers was observed in the far-IR region. Figure 2(b) shows the differential absorption spectrum (ΔA) between with and without application of V_G. Strong noises at around 0.135 eV correspond to the effects of the phonon absorption in the substrate. Data sets are displayed for every 25 V from $V_G = -100$ to 100 V, and the gate electric field induced the intensity change of the S1 transition. Here, we can neglect the heating effect because of the low leakage current between the source/drain and gate electrodes (less than 1 nA for $V_G = 100$ V). As has been well established in the experiments on carrier doping, doped carriers cause bleaching in the S1 transition associated with an enhancement of the Drude absorption in the mid-IR region.[12,13] Conversely, a decrease in the number of charge carriers should result in an increase in S1 absorption. Here, the application of negative (positive) V_G reduced (enhanced) the S1 transition and, as a result, increased (decreased) carrier density in a manner that was consistent with source–drain conductance. This presents direct evidence of carrier accumulation in semiconducting SWNTs, and is qualitatively identical to that in a recent report on electrochemically doped SWNT thin films.[6] It is notable that a small peak shift in the ΔA spectra is attribute to the Stark effect and the detailed analysis will be given elsewhere.[14]

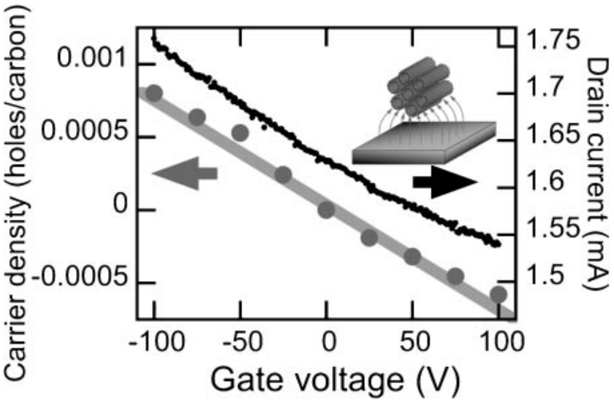

Fig. 3. Gate voltage dependence of estimated carrier density (left) and source–drain current (right). Inset: Schematic of gate electric field concentration on SWNT bundle.

We quantitatively estimated the doped/dedoped carrier density from an optical spectrum, since the intensity of the absorption peak is related to the carrier density. In a potassium-doped SWNT, KC_{27}, this analysis revealed that the 66% reduction of the interband absorption corresponds to a carrier density of 0.037 electrons/carbon.[12] We used this relationship as a standard. The peak intensity of Fig. 2(b) corresponds to a variation (increase or decrease) in the spectrum. The remaining unknown parameter was the absorption intensity of the accumulation layer. In this analysis, we assumed that the depth of the accumulation layer is identical to the diameter of our laser-SWNT bundle, which was estimated to be 11 nm.[12] Since the thickness of the whole film was 25 nm, the intensity of the accumulation layer could be estimated to be 11/25 in Fig. 2(a). Using the standard relation for KC_{27}, we finally derived the carrier density in the SWNT-TFT as a function of gate voltage (Fig. 3).

The linear dependence in Fig. 3 indicates that hole-type carriers are already doped unintentionally in the zero V_G states, and they are modulated by gate voltages as well as the source–drain conductance. From this slope, we obtained the carrier density per gate voltage (7.28×10^{-6}/carbon·V). This is much larger than the value estimated from the parallel-electrode model (8.3×10^{-7}/carbon·V), which is generally used for TFTs. However, if the SWNTs are dispersed with interspacing, the capacitance per tube increases due to the concentration of the gate electric field (see inset of Fig. 3). The calculated carrier density for a single bundle (11 nm) was 4.7×10^{-5}/carbon·V. The experimentally estimated carrier density (7.28×10^{-6}/carbon·V) is between that of the parallel-electrodes model (8.3×10^{-7}/carbon·V) and the single-wire model (4.7×10^{-5}/carbon·V). Thus, we can conclude that the partial isolation of the SWNT increases the carrier density in our TFT.

In conclusion, we measured the electric-field-induced optical changes in the SWNT-TFT as a function of gate voltage. The observation of the carrier accumulation has allowed the direct estimation of the gate-doped carrier density on SWNTs, indicating the field concentration in each bundle. This is the first quantitatively observation of carrier density in SWNT-FETs.

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