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Gate-enhanced exciton-phonon coupling in photocurrent of (6,5) single-walled carbon nanotube based visible sensing field effect transistor

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ABSTRACT

A visible sensing field effect transistor (FET) with a channel length of 100 nm for individual (6,5) single-walled carbon nanotubes (SWCNTs) is fabricated via a selective sorting method using 9,9-dioctyfluorenyl-2,7-diyl–bipyridine (PFO–BPy) polymer. The FET of the (6,5) SWCNTs shows *p*-type behavior with hundreds of on-off ratios and on-state conductivity of 50 ± 4.0 $(\Omega\,m)^{-1}$. In addition, the photocurrent of the FET of the (6,5) SWCNTs in the visible range increases (maximum 200 times at 620 nm) with higher gate voltage. E_{22} transition and PFO-BPy transition are observed in the FET of the (6,5) SWCNTs without application of a gate voltage. Interestingly, exciton-phonon coupled E_{22} transition due to gate-doping (*p*-type), which has been reported in photoluminescence and absorption studies, is expected to occur in the photocurrent of the FET at negatively higher gate voltage (≤ -4 V). In addition, the exciton-phonon coupled E_{22} transition is prominently observable when carrier concentration by gate doping becomes approximately two-hundred sixty times (260 ± 43) larger than carrier concentration without application of a gate voltage. This demonstration would be useful for the development of SWCNT-based visible sensors with gate control in the SWCNT devices.

1. Introduction

Since their discovery [1,2], single-walled carbon nanotubes (SWCNTs) have attracted significant attention from researchers and engineers owing to their unique and superior properties, such as chirality dependent band-gap formation [3]. Semiconducting SWCNTs, which are two out of three of the total SWCNTs [4], are useful materials in applications that utilize their electrical properties, for examples, molecular field effect transistors [5], chemical [6] and optical [7,8] sensors, etc. However, when film SWCNTs are used, separation of the SWCNTs with a certain chirality is necessary for the fabrication of semiconducting devices with uniform band-gaps. There have been lots of developments on the sorting methodology for SWCNTs including electrophoresis [9], density gradient ultra-centrifugation [10,11], chromatography [12,13], selective solubilization, and selective reaction [14]. It was recently reported that polyfluorene (PFO) copolymers can wrap around (6,5) SWCNTs compatible with the structure of the copolymer. Consequently, (6,5) SWCNTs can be separated by centrifugation from unwrapped SWCNTs (SWCNTs of the other chirality). Owing to the development of the sorting methodology, electrical and optical applications that benefit from SWCNTs of one band-gap have been reported, including two-dimensional (2D) arrays of highly sensitive infrared (IR) phototransistors [15,16], broadband photovoltaics [17], bolometric-effect-based photodetectors [18], quasi-ballistic SWCNT array transistors [19], field-effect transistors (FETs) with bottlenecked inter-tube tunneling at low temperatures [20], and visible sensors with wide band-gap oligomer wrapping [17]. However, most applications are focused on the IR response of SWCNTs because the E_{11} transition in SWCNTs is the most efficient. For visible sensor applications, photo-doping from the additive visible responsible polymer is utilized, rather than visible transitions in SWCNTs such as E_{22} transition.

In addition to the sorting methodology used for SWCNTs, deep

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understanding of the opto-electrical properties of SWCNTs is essential for the development of effective visible and IR sensors based on SWCNTs. Interestingly, unique opto-electrical phenomena have been reported in SWCNTs due to their one-dimensional (1D) nature in charge transport [21–23]. For example, multiple exciton generation [23–25], exciton-exciton annihilation [26–29], and exciton-phonon coupled absorption [30] have been reported because strong exciton confinement and phonon coupling are indicated by a narrow diameter and ideal 1D conducting characteristics in SWCNTs. Especially, under a relatively high electrical-field (E-field), excitons and phonons can be more effectively coupled, and exciton-phonon coupled energy bands can be lower and higher depending on the structural symmetry of phonon excitation [31]. Avouris group [32] reported that weaker phonon-assisted sidebands at about 200 meV above the E_{22} transition are observed in the photocurrent of individual SWCNT-FETs. In addition, approximately 200 meV (above) and 140 meV (below) shift of exciton-phonon coupled sidebands in optical transition of (6,5) SWCNTs was reported by Blackburn et al. [33]. On the other hands, Kato et al. [34] also reported that dark exciton transition below the E_{22} transition in the photocurrent of individual SWCNT devices can be red-shifted with E-field application. Due to the visible response of the E_{22} transition, the aforementioned phonon-assisted sideband near the E_{22} transition would be useful for the development of efficient visible sensors based on SWCNTs.

In this article, we report that the photo-transistors of (6,5) SWCNTs have gate-enhanced photoconductivity in the visible range. FETs of (6,5) SWCNTs were fabricated by wrapping with 9,9-dioctyfluorenyl-2,7-diyl–bipyridine (PFO–BPy), and showed a typical *p*-type behavior. Interestingly, the FETs showed hundreds of on-off ratios and on-state conductivity (σ) of 50 ± 4.0 $(\Omega\,m)^{-1}$. While E_{22} transition and PFO-BPy transition were observed without the application of a gate voltage, both red and blue-shifted E_{22} transitions were detected and assumed to be energy band modifications resulting from exciton phonon-coupling at relatively high gate voltages. Moreover, it is proposed that increase of carrier concentration more than two-hundred sixty times would be required for the prominently observable exciton phonon-coupled E_{22} transitions. Our demonstration of the gate-enhanced photocurrent of the SWCNT-FETs in the visible range would be beneficial for the development of wavelength-controllable visible sensors based on SWCNTs.

2. Experimental

As the first step in sorting (6,5) SWCNTs, 1 mg of commercially available SWCNTs (CoMoCAT, Sigma-Aldrich Inc.) and 3 mg of PFO-BPy (ADS153UV, American Dye Source Inc.) were mixed in 3 mL of toluene solution by sonication for one hour. To remove the SWCNTs not bound to PFO-BPy, the mixed solution was centrifuged (12700 rpm for one hour), and the supernatant SWCNT solution was extracted. Excess PFO-BPy molecules were filtered through a membrane filter (GVHP04700, $\phi = 220$ nm, Sigma–Aldrich Inc.) [35]. The PFO-BPy-wrapped (6,5) SWCNTs were dispersed onto a silicon dioxide (SiO_2)-coated highly-doped silicon substrate ($SiO_2 = 300$ nm, *p*-type, $\sigma = 0.500–0.735$ S/cm, LG SILTRON Inc.) using an e-beam lithography-labeled marker system. By means of e-beam lithography (JBX9300FS, Jeol, NanoFab Center, Korea) and sequential e-beam evaporation (El-5, ULVAC, NanoFab Center, Korea), Pd with a thickness of 30 nm was deposited on the PFO-BPy-wrapped (6,5) SWCNTs as source-drain electrodes. Additionally, a back gate electrode connection was established with Ag wire ($\phi = 0.125$ mm, Good fellows, USA) and Ag paste (D–500, DOTITE) after scratching away the SiO_2 dielectric layer on the highly-doped silicon substrate. The gate-dependent opto-electrical properties of the PFO-BPy-wrapped (6,5) SWCNT FETs were measured with a highly sensitive dual channel source measuring unit (2634B, Keithley Instrument, Inc. Solon, USA) and a home-built light irradiating system. The light irradiating system is composed of a Xenon arc lamp (500 W, 67005, Newport Inc, USA), a 1/8 m monochromator (10 nm grating, CM110, Compact Spectral Products Inc, USA), and a focusing lens. Monochromatic light power at the sample position is 5–9 mW in the range of 400–700 nm. Characterization of the PFO-BPy wrapped (6,5) SWCNTs was carried out with tapping mode atomic force microscopy (AFM) (Dimension ICON, Bruker Inc, USA), UV–vis absorption (V–670, JASCO), photoluminescence (PL) (FluorologR-3 with FluorEssence, Horiba Jobin Yvon), Raman spectroscopy (NRS–5100, JASCO), scanning electron microscopy (SEM) (Supra 40VP, Cal Zeiss Inc., Germany), ultraviolet photoelectron spectroscopy (UPS) (ESCALAB 250XI, Thermo Fisher Scientific Inc, USA), and cyclic voltammetry (WPG10, WonATech, Korea) measurements.

3. Results and discussion

Fig. 1(a) shows the tapping mode AFM topography (a–I) and peak force error (a–II) images of the PFO-BPy-wrapped (6,5) SWCNTs dispersed onto e-beam marker-labeled highly-doped silicon substrate. Averaged length and diameter of the PFO-BPy-wrapped (6,5) SWCNTs are characterized from histograms obtained from 428 (length) and 357 (diameter) numbers of sampling. In the results, averaged length of the PFO-BPy-wrapped (6,5) SWCNTs is 580 ± 290 nm, and diameter of that is 0.97 ± 0.27 nm, respectively. A cross-sectional line-profile of the PFO-BPy-wrapped (6,5) SWCNTs is displayed in the inset of Fig. 1(a–I). It can be confirmed by absorption (Fig. 1(b)) and PL (Fig. 1(c)) characterization that sorting of the (6,5) SWCNTs based on PFO-BPy wrapping was successful. According to the previous report [35], 91.2 ± 1.2% of (6,5) SWCNTs and 8.8 ± 1.2% of (7,5) SWCNTs can be obtained with small content (<0.1%) of (8,3), (8,4), and (7,6) SWCNTs through the sorting of SWCNTs (CoMoCAT) using PFO-BPy in toluene. In Fig. 1(b), the E_{11} and E_{22} transitions of the (6,5) SWCNTs are clearly visible at 994 nm and 574 nm [36,37]. The saturated absorption less than 400 nm originates from absorption of PFO-BPy materials (Fig. S1(c)) [38,39]. The weak peaks at 550 nm and 850 nm are related to exciton-phonon sidebands of (6,5) SWCNTs (denoted as PS in Fig. 1(b)) [40,41]. The peaks at 650 nm and 1050 nm would be E_{22} and E_{11} peaks of (7,5) SWCNTs, respectively (denoted as (7,5) in Fig. 1(b)) [42]. The absence of obvious peaks other than those for the E_{11} and E_{22} transitions proves that (6,5) SWCNTs are dominant in the sample badge. In addition, PL mapping of the sample shows a single strong PL emission at 1000 nm with 574 nm of excitation, which also confirms that (6,5) SWCNTs mainly exist. The weak satellite peaks (marked by " × " in Fig. 1(c)) near the PL peak at 1000 nm and ~1100 nm of emission were previously assigned as phonon sidebands [30,33,37,43,44]. However, the weak PL peak at ~1100 nm of emission can be also related to oxygen containing defects on the nanotube side wall [45]. In addition to sorting the (6,5) SWCNTs, the existence of PFO-BPy molecules can be demonstrated by the Raman spectra of the PFO-BPy-wrapped (6,5) SWCNTs dispersed on the silicon substrate (Fig. 1(d)). Fig. 1(d) shows that the visible peaks are identifiable as PFO molecule vibrations with the "G" and "D" peaks of SWCNTs. Moreover, the radial breathing mode (RBM) of the (6,5) SWCNTs is observed in the Raman spectrum (Inset of Fig. 1(d)). It was reported that RBM in the regions of 240–300 cm^{-1} and 150–240 cm^{-1} is attributed to the semiconducting and metallic SWCNTs, respectively [35]. Hence, the weak peaks near 275 cm^{-1} could be RBMs of other type of SWCNTs such as (7,5), and the peak at 230–275 cm^{-1} could originate from metallic SWCNTs. Overall the optical characterization of the sample