Near-infrared photodetection using random networks of single-walled carbon nanotubes with asymmetrical work-function electrodes

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Abstract

We investigate the use of random networks of single-walled carbon nanotubes for near-infrared photodetection. By increasing the number of nanotubes between asymmetrical work-function electrodes using dielectrophoretic assembly, the effect of Fermi-level pinning of nanotube-Schottky contacts was revealed in the linear current-voltage characteristic. The extracted device resistance showed an abrupt drop when the numerous intertube junctions formed densely packed networks in the electrode channel. Under the excitation of a near-infrared laser, we performed the photocurrent measurement at ambient temperature at different light powers. Our devices with densely packed nanotube networks showed enhanced photoconductive detection of responsivity, detectivity, and detection response. This is attributed to the increase in the photoabsorption area, the decrease of the channel resistance, and the formation of continuous conducting paths for high-efficient charge percolation. The photoconductive responsivity of up to 8.0 μA W⁻¹ was found with a detectivity of about 4.9 × 10⁵ cm Hz¹/² W⁻¹, which is 4 orders of magnitude greater than that achieved in the channel with individual nanotubes deposited and comparable to that of suspended nanotube bolometers. The densely packed nanotube devices had a detection response of ~ 4 ms under a finite bias that can be explained by the short-diffusion length of the photoexcited electrons and holes. However, the decrease in the photocurrent with time observed in our devices that exhibited photovoltaic characteristics indicates that electron-hole pair recombination in the nanotube networks occurs with differing characteristic time scales of the injected electrons and holes.

1. Introduction

Single-walled carbon nanotubes (SWCNTs) have shown many outstanding electrical properties and a broad-wavelength absorption spectrum for the development of future optoelectronic devices [1–4] including high-performance field-effect transistors [5, 6], gas sensors [7, 8], and biosensors [9, 10]. Most techniques realized so far have exploited semiconducting SWCNTs (s-SWCNTs) or multi-walled carbon nanotubes (MWCNTs) assembled between lithographically patterned microelectrodes on a silicon substrate. The formation of nanotubes in the device channels can be tuned from individually well-aligned to randomly-oriented arrangements with top-down and bottom-up approaches of nanofabrication processes. The commonly used top-down approach is to create a simple SWCNT-field-effect transistor (SWCNT-FET) using symmetrical work-function metal electrodes [11–13]. However, the techniques are limited to batch-to-batch fabrication, and some of them are not compatible with soft substrates due to the requirement of high-temperature grown SWCNTs. On the other hand, the self or directed assembly of nanotubes suspended in aqueous solution offers the possibility of nanoscale-device manipulations with low cost and ease of fabrication [14, 15]. Thus, the quality...
of the devices fabricated by the solution-processed technique is subject to the purity of the nanotubes and the mixtures of semiconducting and metallic properties [16]. Furthermore, the technique can be deployed on a variety of substrates with the capability to control the number of nanotubes on a large-scale manipulation, enabling more complex circuits to be realized.

Despite its ease of fabrication, one of the main obstacles of the bottom-up approach in the solution-processed technique is to align a large number of nanowires, nanorods, or nanotubes for assembling high-efficiency photodetectors. In particular, when the channel length \( L \) of the device is greater than material length \( L_\text{ch} \) [17], random networks of the materials tend to form between source and drain electrodes. As a consequence, the electronic properties of the device depend not only on the quality of materials but also on the charge percolation along the channel that is characterized by the percolation density \( \rho = 4.236^2/\pi L^2 \) [18]. Therefore, the study of percolation transport in random networks could provide an understanding of the device performance in association with charge-carrier mobility, diffusion length, and material density.

In this work, we experimentally characterize the electronic properties of random networks of SWCNT photodetectors implemented using asymmetrical work-function metal contacts by a dielectrophoretic technique. Low and high work-function metals (Al and Au) are used for Schottky and ohmic contacts to the nanotubes, respectively. With this technique, the number of nanotubes in the device channel can be varied from a single few nanotube to a densely packed network. We measure the photocurrent of the devices under the excitation of a near-infrared laser (975 nm) and evaluate their responsivity, detectivity, and time response. We also determine the effect of the number of nanotubes on these indicators of performance. The enhanced photocurrent observed in a channel containing high-density continuous nanotube networks is due to the increase in the photoabsorption area and lower channel resistance.

### 2. Experimental considerations

Our SWCNT photodetector devices are based on a barrier-free bipolar diode (BFBD) structure that exploits asymmetrical metal contacts to the SWCNTs. Low and high work-function metals (Al and Au) were used to contact the nanotubes at opposite sides to form Schottky and ohmic contacts at Al- and Au-nanotubes, respectively, by dielectrophoretic assembly (DEP). As a consequence, the device behaves as a p-i-n photodiode where \( p \) and \( n \) conduction is achieved in high and low work-function metals, respectively [19–21]. The devices were prepared on a SiO\(_2\)/Si substrate using high-purity semiconducting SWCNTs at an initial concentration of 10 \( \mu \)g ml\(^{-1}\) in toluene (NanoIntegris Inc., IsoNanotube-S of 99.9% s-SWCNT [22]). The substrate consisted of a 160 nm thick oxide layer thermally grown on a p-doped Si substrate with a thickness of ~500 \( \mu \)m. An array of Al electrodes (4 pairs in each chip, see figure S1(a) (available online at stacks.iop.org/MRX/8/066303/mmedia)) of supplementary material (SM) was lithographically defined on the substrate by optical alignment followed by metallization and lift-off process. Each of the pre-defined Al-Al electrode pairs possessed a sharp-end separation of 10 \( \mu \)m (figure S1(b)). The center-to-center of each pair was 200 \( \mu \)m apart on a chip of 6 mm by 6 mm. The Al electrode (60 nm thick) was thermally deposited on the Ti/TiN (20/20 nm thick) adhesion layers. We used an Al electrode (low work-function metal, \( \phi_{\text{Al}} \approx 4.28 \) eV [23]) with the SWCNTs (\( E_F \approx 5.01 \) eV [24]) to create a Schottky barrier for holes at the Al-nanotube contact [25]. For the formation of an ohmic contact to the nanotubes, a high work-function metal, namely, Au (\( \phi_{\text{Au}} \approx 5.10 \) eV [23]) was lithographically aligned on top of one end of each Al pair. This was followed by metal deposition of Au (20 nm), as shown in figure S1(c). This Au contact is rectangular (10 \( \mu \)m by 40 \( \mu \)m) to optimize the gradient of the electric field across the device channel [26]. After the lift-off of the Au layer, asymmetrical work-function metal contacts (a Schottky barrier at one end and ohmic contact at the other) were obtained with a channel length reduced to \( L_{\text{ch}} \approx 3 \) \( \mu \)m. The reduced \( L_{\text{ch}} \) is however 3 times larger than the average length of the nanotubes \( (L_{\text{CNT}} \approx 1 \) \( \mu \)m) which had a diameter \( (d_{\text{CNT}}) \) of 1.4 nm [22], which could result in random networks of the nanotubes in the device channel. To achieve such asymmetrical metal contacts, one needs one-step lithographical alignment on top of the pre-defined electrode. Next, the surface treatment of the device was performed by a plasma clean under reactive-ion etching (RIE) for the improvement of the contact angle.

The formation of random networks of the nanotubes in the Al-Au electrodes was achieved by applying a droplet containing 3 \( \mu \)l of nanotubes suspended in toluene at the center of the chip with the application of a 1 MHz 10 \( V_{\text{p-p}} \) AC voltage using a function generator (Agilent 33210A), as shown in figure 1(a). The oscilloscope (DSO-X 2002A Agilent Technologies) was connected to the DEP circuit for monitoring the assembling signals. In this work, we kept the DEP time to 2 min for each assembling process with four repetitions. Immediately after the application of the AC excitation, the chip was blown dry with nitrogen gas (figure 1(b)). By controlling the nanotube concentration, assembling time, frequency, amplitude of the AC signal, and geometry of the electrodes, we could vary the number of the nanotubes in the device channels of each chip simultaneously. This DEP technique enables the fabrication of SWCNT devices with a simple electronic setup on a stable parametric
Figure 1. (a) A schematic diagram illustrating the DEP assembly using an AC voltage applied across a pair of electrodes. (b) The random-nanotube networks bridge the electrodes after the application of the AC voltage. (c) A set of instruments required in this work, comprising an oscilloscope, a function generator, and a high-stability electronic probe tester. (d) An actual image of the DEP assembly showing a droplet of SWCNTs and the electrical contacts.

Figure 2. Scanning electron microscope images of the assembled nanotubes by the DEP technique between Al-Au electrodes of channel length $L_{ch} \approx 3 \mu m$ for nanotube concentrations of (a) 0.01, (b) 0.11, (c) 0.21, and (d) 0.42 $\mu g/ml$. The scale bar in each image equals 1.0 $\mu m$. 
The variation in the number of nanotubes and the formation of random networks are shown in the scanning electron microscope (SEM) images (figure 2). In figure 2(a), the lowest nanotube concentration (0.01 μg ml⁻¹) was used in the DEP assembly. It shows a small number of intertube junctions in the channel. When the number of nanotubes increased, the distance between two adjacent junctions became shorter and the channel formed densely packed networks with random alignments of the nanotubes (figure 2(d)).

In general, the electronic properties of the random-nanotube networks can be determined by the percolation density and the waviness of the nanotubes [17, 18, 27]. Charge percolation through the networks depends on the number of the conducting paths. Charges can percolate from tube to tube if the area density (ρ) of the nanotube exceeds the percolation density (ρ_eff), i.e., ρ > ρ_eff, which gives rise to a continuous film. The device resistance decreased significantly as the number of nanotubes increased. For a fixed channel length (in this work, $L_{ch} \geq 3$ $L_{CNT}$), the percolation density could be as low as $\rho \propto 1/L_{ch} = 0.11 \mu m^{-2}$ with the formation of homogeneous nanotube networks expanded in the channel. Random networks of nanocomposite thin-film transistors have been studied to determine charge-carrier mobility ($\mu$) in long device channels [28–31]. However, these transistors with symmetrical work-function metals for source and drain electrodes could not yield a high sensitivity for photodetection.

In regards to the waviness of the nanotubes in the channel (defined by the curl ratio, $\lambda = L_{CNT}/L_{eff}$, where $L_{eff}$ is the effective length between two ends of the tubes.), $L_{eff}$ can determine the electrical properties of the device. The conductivity ($\sigma$) of the channel increases with decreasing waviness, meaning that $L_{eff} \gg L_{CNT}$. The electrical conductivity of the channel can be described by $\sigma \propto \lambda^{-\gamma}$ with $\gamma$ ranging from 2.2–2.6 in 2D networks and 1.7–2.0 in bulk 3D networks [27, 32]. This suggests that high-efficient charge percolation in random networks or nanocomposites can be achieved in the channel with less waviness of the nanomaterials. For nanotubes that are much shorter than the channel length ($L_{CNT} \ll L_{ch}$), numerous inter-tube junctions have been formed as densely packed networks, suggesting that $L_{eff} > L_{CNT}$ with an expansion across Al-Au electrodes. As a result, the channel can be viewed as a homogeneous film of nanotubes. Our experimental findings confirmed that the increase of the device performance was a result of the increased number of nanotubes in the channel and the lower waviness of them.

To further verify the electronic properties of the random-nanotube networks in the channels, we performed two-terminal DC measurements using Keithley 2450 and 2401 source meter units inside a metal-screened box. Here, the bias voltage was applied to the Au contact by grounding the Al contact. The I-V characteristics of all investigated devices are displayed in figure 3(a). In this work, the devices exhibiting the rectifying behavior with a forward bias ($I_{F}$) and reverse bias current ($I_{R}$) such that $I_{F}/I_{R} \gg 10^2$ are obtained for Devices A—C (low nanotube concentrations of 0.01–0.11 μg ml⁻¹). Devices D—F assembled with high nanotube concentrations

3. Results and discussion

The simulated I-V characteristics of a diode when a variable resistor of $R_p$ is connected in parallel to the circuit. $R_p$ varies from 0.1 $R_s$ to $10^4 R_s$. The inset shows the diode equivalent circuit diagram under reverse-bias configuration.

**Figure 3.** (a) The I-V characteristics of the SWCNT devices fabricated by DEP assembly for various nanotube concentrations. The circuit diagram shows the connection of $V_{bias}$ across the Al-Au electrode channel. The inset shows rectifying diode characteristics for nanotube concentrations of 0.01, 0.05, and 0.11 μg ml⁻¹ with the shaded area showing the linear I-V regime for the estimation of channel resistance, $R_c$. (b) The simulated I-V characteristics of a diode when a variable resistor of $R_p$ is connected in parallel to the circuit. $R_p$ varies from 0.1 $R_s$ to $10^4 R_s$. The inset shows the diode equivalent circuit diagram under reverse-bias configuration.
is the reverse-bias current, \( I_{\text{r}} \), which increases with the increase in nanotube concentrations. However, a critical concentration of \( \mu = 0.21 \) to 0.42 results in linear conducting behavior obtained at a critical concentration of \( C \approx 0.12 \pm 0.02 \mu g \text{ ml}^{-1} \) at the value of the channel resistance \( R = 3.5 \pm 0.1 \Omega \). The measured current evaluated at \( V_{\text{bias}} = +1.5 \text{ V} \) is plotted as a function of \( 1/R \) (top-right axis) showing the increase of the current with the increase in nanotube concentrations.

Figure 4. A semi-log plot of \( R \) versus nanotube concentration (bottom-left axis) indicates a crossing point between the rectifying and conducting behavior obtained at a critical concentration of \( C \approx 0.12 \pm 0.02 \mu g \text{ ml}^{-1} \) at the value of the channel resistance \( R = 3.5 \pm 0.1 \Omega \). The measured current evaluated at \( V_{\text{bias}} = +1.5 \text{ V} \) is plotted as a function of \( 1/R \) (top-right axis) showing the increase of the current with the increase in nanotube concentrations.

Table 1. The extracted parameters using equations (1)–(3) of all investigated devices in this work.

| Device | \( \text{conc.} \) (\( \mu g \text{ ml}^{-1} \)) | \( \eta \) | \( R \) (\( \Omega \)) | Detection principle\( ^a \) | \( V_{\text{bias}} \) (V) | \( \tau \) | \( R_l \) (AW\(^{-1} \)) | \( D^* \) (cm Hz\(^{1/2} \text{ W}^{-1} \)) |
|--------|-----------------|---|-----|----------------|----------------|-----|-----------------|-----------------|
| A      | 0.01            | 20.1 | 2400 | PV             | -0.01          | N/A | N/A             | N/A             |
| B      | 0.05            | 9.5  | 64.7 | PV             | -0.01          | 2.6 s| 11.0 \times 10^{-10} | 6.1 \times 10^{4} |
| C      | 0.11            | 4.3  | 7.2  | PV             | -0.01          | 6.6 s| 8.5 \times 10^{-10} | 4.7 \times 10^{4} |
| D      | 0.21            | N/A  | 4.0  | PC             | +2.0           | 6.65 ms| 1.4 \times 10^{-6} | 8.5 \times 10^{4} |
| E      | 0.30            | N/A  | 3.9  | PC             | +2.0           | 4.46 ms| 1.3 \times 10^{-6} | 6.6 \times 10^{4} |
| F      | 0.42            | N/A  | 3.2  | PC             | +2.0           | 3.56 ms| 8.0 \times 10^{-6} | 4.9 \times 10^{4} |

\( ^a \) Assembling concentration (\( \text{conc.} \)).

\( ^b \) Photodetection performance under laser illumination (975 nm, 435 mW) showing time response, responsivity, and detectivity of all investigated devices with photovoltaic (PV) and photoconductive (PC) detections.

\( (>0.12 \mu g \text{ ml}^{-1} \) result in linear \( I-V \) curves. The data obtained from Devices A, B, and C could be fitted well by the modified diode equation in the thermionic emission model [33],

\[
I(V) = I_0 \left[ \exp \left( \frac{e(V - IR_s)}{\eta kT} \right) - 1 \right] - I_{\text{sc}},
\]

where \( I_0 \) is the reverse-bias current, \( \eta \) is the diode ideality factor, and \( e \), \( k \), and \( T \) are the electric charge, Boltzmann constant, and temperature, respectively. The offset current \( (I_{\text{sc}}) \) in equation (1) refers to the short-circuit current when the devices are illuminated. The shaded region in high bias \( (V_{\text{bias}} = 1 - 2 \text{ V}) \), shown in the inset of figure 3(a) of Device A to C, was fitted to Ohm’s law to estimate the channel resistance \( (R) \) under the forward bias, which approximately equals the series resistance \( (R_s) \) obtained in equation (1). Here, \( R_s = R_c + R_{\text{CNT}} \), where \( R_c \) is the contact resistance between metal and nanotube, and the sheet resistance, \( R_{\text{CNT}} = \rho_{\text{CNT}} L_A / Wd \), where \( W, d \), and \( \rho_{\text{CNT}} \) are channel width, film thickness, and film resistivity, respectively. In our two-terminal DC measurement, the value of \( R_c \) is inaccessible but depends on the metal-nanotube contact area, the intertube junction area, and the barrier height at the metal-nanotube contacts. However, a theoretical study has shown that the contact resistance between nanotubes is approximately 3.4 M\( \Omega \) [34]. The value of \( R_{\text{CNT}} \) could be determined by the physical dimension of the electrode channel and the intrinsic properties of the nanotubes that result in \( \rho_{\text{CNT}} \). Table 1 summarizes \( R \) and \( \eta \) that are obtained in the \( I-V \) characteristics of figure 3(a) and the estimation using equation (1).

By further increasing the nanotube concentration from 0.21 to 0.42 \( \mu g \text{ ml}^{-1} \) (Devices D—F), the measured current showed a linear dependence of the bias voltage, permitting the estimation of \( R \) by Ohm’s law suggesting that \( R \) is dominated by \( R_{\text{CNT}} \) in the device channel. We see that the experimental results are identical to the
numerical simulations when a resistor of $R_p$ was connected in parallel to the shunt resistance, $R_{sh}$. As shown in figure 3(b) and its inset, the linear I-V curves followed by Ohm’s law are obtained by using the LTspice program [35]. When the value of $R_p$ is much less than $R_{sh}$, we assume that $R_p$ is very small. The curves show perfect rectifying diodes when $R_p$ is $10^4 R_{sh}$, where $R_{sh}$ is set to 3.5 MΩ. The decrease in $R$ indicates the increase of the material thickness in a fixed channel length as $d$ and $W$ increase.

We found no significant difference in $\mu$ as shown 0.16 and 0.26 cm$^2$ V$^{-1}$ s$^{-1}$ in Device B (0.05 $\mu$g ml$^{-1}$) and Device F (0.42 $\mu$g ml$^{-1}$), respectively (see data and the calculation in section S2 of SM). Thus, the increase of the electrical conducting in the random-nanotube networks could be verified by the number of nanotubes in the channel, in contrast to the carrier mobility. The appearance of the rectifying behavior in such an asymmetrical Schottky contact structure of low-nanotube concentrations (0.01–0.11 $\mu$g ml$^{-1}$) shows the existence of interface dipoles at metal-nanotube contacts, resulting in the depinning of the Fermi level at the metal-nanotube contact [36]. This is unlikely to happen in a bulk nanotube-metal contact since its barrier height is fixed by the neutrality level of the interface state ($E_F - E_g$). As a result, the Fermi level is said to be pinned inside the nanotubes. Therefore, the choice of low and high work-function metals has not affected the creation of asymmetrical barrier heights for charge injections in the densely packed networks of the nanotubes. This effect can be seen in most metal-semiconductor junctions with bulk-contact structures [37–39]. Furthermore, as the number of nanotubes increases in the random networks, the depletion width ($W_d = \sqrt{2\varepsilon\phi_h/n_d\epsilon}$, where $\varepsilon$ is the dielectric constant of the nanotube and $\phi_h$ is the barrier height) can be reduced by increasing the number of dopants ($n_d$) for a given $\phi_h$ [40, 41]. Therefore, the lower the $W_d$, the more charge injections at the nanotube-metal contacts. As a consequence, the tunneling current dominates the thermionic emission current of a diode in the densely packed networks, resulting in the I-V characteristics following Ohm’s law.

We analyzed the electronic properties of the random nanotubes in the channel by plotting $R$ of all investigated devices as a function of the nanotube concentrations. As shown in figure 4 (bottom-left axis), $R$ decreases rapidly as the concentration increases and remains constant at $\sim 3.5$ MΩ for the highest concentration (0.42 $\mu$g ml$^{-1}$). The decrease of $R$ in the densely packed networks indicates the formation of bulk nanotube-metal contacts as shown by two solid lines, which is confirmed by the increase of current (in the top-right axis at a fixed bias of +1.5 V). The slope of the lines gives the critical concentration of $C = 0.12 \pm 0.02$ $\mu$g ml$^{-1}$.

To demonstrate the photodetection characteristics, a near-infrared (NIR) laser with a wavelength of 975 nm was used to excite charge carriers in the nanotubes. According to the absorption spectrum of the ultraviolet-visible (UV-VIS) spectroscopy (figure S3) and the material’s datasheet [22], the absorption peak was centered at a wavelength of 940 nm with a broad spectrum of ±100 nm. Thus, the use of light with wavelengths below 840 nm and above 1040 nm is considered as the cut-off wavelength for the NIR photodetection in this experiment. Therefore, our photexcitation of the wavelength 975 nm of the laser is near the highest photo absorption with the calculated photon energy ($E_{ph}$) of 1.27 eV which is higher than the energy gap ($E_g$) of the SWCNTs given by $E_g = 0.84/d_{CNT} \approx 0.6$ eV [42], where the nanotube diameter ($d_{CNT}$) is 1.4 nm. As a result, the excitation by 975 nm laser leads to high-efficient carrier generation in this experiment.

Under the NIR illumination, we demonstrated the photodetection capability of the random-nanotube networks in the DEP assembled devices. We found the photocurrent increased with the number of nanotubes in the channel. The measurement of the photocurrent gives the device photoresponsivity ($R_i$) and detectivity ($D^*$),
which represent the photodetection performance of a photodetector via:

\[ R_P = \frac{I_p}{P_{\text{inc}}} \]  
\[ D^* = \frac{\sqrt{A}}{\text{NEP}} \]  

where \( I_p \) is the photocurrent defined by the offset of the measured current of different light conditions, \( I_p = |I_{\text{ON}} - I_{\text{OFF}}| \), and the noise equivalent power \( \text{NEP} = \sqrt{S_I} / R_N \), where \( S_I \) is the current noise spectral density. At zero-bias voltage, \( I_{\text{ON}} \) is the measured current given by equation (1) with \( I_{\text{sc}} \approx 0 \) and \( I_0 \approx 0 \) under the illumination of light (laser 'ON' condition), whilst \( I_{\text{OFF}} \) refers to \( I_{\text{ON}} \approx 0 \) when the device was measured in the 'dark' (laser 'OFF' condition). \( P_{\text{inc}} \) is the incident power on the active area \( (A) \) of the device including the contact pads (see calculation in section S4 of SM).

In figure 5(a), the I-V characteristics of Device B assembled with a nanotube concentration of 0.05 \( \mu \text{g ml}^{-1} \) were taken under the excitation of the NIR laser. The data plotted in the logarithmic scale shows the measured current at two different light conditions. The results indicate a clear difference in the measured current from nearly zero to \(-2 \text{ V}\), leading to the photocurrent \( I_p \approx 1 \text{nA} \). This detection principle exhibits the photovoltaic (PV) detection characteristic with an open-circuit voltage \( (V_{\text{oc}}) \) obtained at \( \sim 20 \text{ mV} \). The solid lines are fitted by using equation (1). The inset is their linear-scale plots that show a negative \( I_{\text{sc}} \) at \( V = 0 \), in correspondence to the data in the main graph. In figure 5(b), the linear I-V curves of Device F assembled using a nanotube...
Table 2. A comparison of the detection performance in carbon nanotube-based photodetectors.

| NANOtube DEVICES [REF.] | Contact Structure\(^c\) | Detection Characteristics\(^d\) | Light Intensity [W cm\(^{-2}\)] (Wavelength [nm]) | \(\tau\) | Responsivity | Detectivity [cm Hz\(^{1/2}\) W\(^{-1}\)] |
|-------------------------|--------------------------|-------------------------------|-----------------------------------------------|--------|---------------|-----------------------------------|
| SWCNT networks [This work]\(^e\) | BFBD (Asm) | PV | 2.4 (975) | 2.6 s | 1.1 nA W\(^{-1}\) | 6.1 \(\times\) 10\(^1\) |
| SWCNT networks [This work]\(^e\) | BFBD (Asm) | PC | 2.4 (975) | 3.6 ms | 8.0 \(\mu\)A W\(^{-1}\) | 4.9 \(\times\) 10\(^3\) |
| Individual SWCNT [54] | Sym | PV | 7.1 (1550) | 4 ms | 0.18 A W\(^{-1}\) | N/A |
| Well-aligned SWCNTs [55] | BFBD (Asm) | PV | 1570 (785) | N/A | 98 \(\mu\)A W\(^{-1}\) | 1 \(\times\) 10\(^7\) |
| SWCNTs/PC\(_{71}\)BM [43] | BHJ (Asm) | PV | 0.1 (1010) | 40 ms | 0.02 A W\(^{-1}\) | 2 \(\times\) 10\(^9\) |
| SWCNTs/polycarbonate [51] | Sym | PC | 0.7 (1300) | 40 ms | 0.4 \(\mu\)A W\(^{-1}\) | N/A |
| SWCNTs/P3HT [2] | BHJ (Sym) | PC | 1.6 \(\times\) 10\(^{-2}\) (1000) | 1.4 ms | 16 mA W\(^{-1}\) | 2.3 \(\times\) 10\(^8\) |
| MWCNT/graphene [56] | BHJ (Sym) | PC | 3.0 \(\times\) 10\(^{-2}\) (1000) | 1.5 ms | 1000 V W\(^{-1}\) | 1.5 \(\times\) 10\(^7\) |
| Suspended SWCNTs [49] | Sym | Bolometer | 3 \(\times\) 10\(^{-3}\) (1300) | 50 ms | 150 V W\(^{-1}\) | 4.5 \(\times\) 10\(^7\) |
| Suspended MWCNTs [50] | Sym | Bolometer | 36 (940) | 60 ms | 110 V W\(^{-1}\) | 4.0 \(\times\) 10\(^6\) |

\(^c\) BFBD: barrier-free bipolar diode, BHJ: bulk heterojunction, Asm: asymmetrical metal electrode, Sym: symmetrical metal electrode.

\(^d\) The detection characteristics with photovoltaic (PV), photoconductive (PC), and bolometric behavior.

\(^e\) The PV detection principle (Device B) with nanotube concentration = 0.05 \(\mu\)g ml\(^{-1}\) at \(V\)\(_{bias}\) = −0.01 V.

\(^f\) The PC detection principle (Device F) with nanotube concentration = 0.42 \(\mu\)g ml\(^{-1}\) at \(V\)\(_{bias}\) = +2.0 V.
concentration of 0.42 μg ml⁻¹ show the change in the device resistance. The photocurrent of this device was \( I_P \approx 330 \text{ nA} \) with the photoconductive (PC) detection under the bias voltage of +2 V which was two orders of magnitude higher than that of Device B.

\( R_1 \) and \( D \) as given by equations (2) and (3) are used to assess the detection performance. For all devices measured here, the values of \( R_1 \) and \( D \) of the devices were found in the range \( 10^{-16} \) to \( 10^{-6} \) A W⁻¹ and \( 10^3 \) to \( 10^6 \) cm Hz⁻¹ W⁻¹, respectively, after normalizing with the photoabsorption area \( A \) (see the discussion of \( D \) and NEP in the following sections). As summarized in table 1, the data show that \( R_1 \) and \( D \) are inversely proportional to the channel resistance. In Device A, the photocurrent was impossible to achieve in our measurement setup, due to insufficient light absorption and the high device impedance. The results shown in figures 5(a) and (b) suggest that a considerable increase in \( R_1 \) and \( D \) could be obtained by further decreasing the channel resistance, which depends on the intrinsic properties of the nanotubes.

The temporal response of the devices was measured via a load resistor of \( R_L = 10 \text{ kΩ} \) to convert the photocurrent into a photovoltage signal displayed by an oscilloscope (input impedance of 1 MΩ and 11 pF). The excitation voltage with a frequency of 1.4 Hz from the wave generator of the oscilloscope was used to modulate the radiation of the laser. Thus, the signal in the voltage response could be converted to the current response after dividing by \( R_L \). For the estimation of the time response (\( \tau \)), the rising signal was estimated between 10% and 90% of the amplitude in a period of the laser modulation.

As shown in figure 6(a), \( I_{p1} \) from Device B shows a small increase at a bias of −0.01 V. This device yielded a \( \tau \) of 2.6 s, obtained at a laser power of 435 mW. In Device D, E, and F, we found the reduction of the time response of the devices assembled with the nanotube concentrations of 0.42 \( \mu \text{g ml}^{-1} \) (Device F), as shown in figure 6(b). The graph shows that \( \tau = 3.56 \text{ ms} \) in Device F, which is less than that reported by some uncooled-bolometer devices using nanocomposite materials [43–45].

The decrease in the photocurrent observed in Device B can be discussed in the context of the electrons (e⁻) and hole (h⁺) pair recombination. As shown in figure 6(a), the device has little nanotube deposition in the electrode channel. After photoabsorption in the SWCNTs, e⁻–h⁺ pairs are generated in the entire nanotubes. The e⁻ and h⁺ are separated by a built-in electric field in the depletion region at the Al-nanotube contact where h⁺ is injected into the nanotubes, resulting in the photocurrent with a PV characteristic at zero-bias voltage. The recombination of e⁻ and h⁺ takes place outside the depletion region but in the SWCNT networks. As we applied a small bias of \( V_{bias} = -0.01 \text{ V} \), the injected h⁺ from the Al-nanotube contact recombines with the injected e⁻ through the diffusion process in the SWCNTs because of this bias. If \( \Delta n_0 \) characterizes the time-dependent number of photogenerated h⁺ swept into the nanotubes by the built-in electric field and \( \Delta n_0 \) defines the number of injected e⁻ by the small bias via the diffusion process, the net charge carriers injected into the nanotubes will suppress the number of holes by the injected electrons from the small bias. The photocurrent of the nanotubes is described by \( \Delta n(t) = \Delta n_0 \exp \left(-t/\tau_0\right) = \Delta n_0 \exp \left(-t/\tau_e\right) \), where \( \tau_0 \) and \( \tau_e \) characterize the time response of the h⁺ and e⁻, respectively. Therefore, the photocurrent of the device is a competition between the injected h⁺ and e⁻. Furthermore, as there are few nanotubes present in the device channel, e⁻ cannot percolate through the random networks efficiently, leading to a slow time response in comparison to the fast-injected h⁺ assisted by the built-in electric field at the Al-nanotube junction. Since the depletion width of the junction is much smaller than the channel length and h⁺ is injected into the nanotubes by the built-in field, this results in \( \tau_0 \ll \tau_e \). Thus, the photocurrent observed in Device B with a PC characteristic decreased with time in a favor of the injected electrons through the diffusion process under a small bias. A similar effect has also been observed in graphene/silicon photodetectors [46].

The decrease in the photocurrent with time, however, is not observed in Devices D—F that are operated with a PC characteristic under a large bias voltage (+2 V). These devices possess a large number of nanotube depositions between electrodes with bulk nanotube-metal contacts, resulting in no depletion region and hence no built-in electric field. In these devices, e⁻–h⁺ pairs are created by photoexcitation of the photons with an energy higher than the SWCNT energy gap. After the photoexcitation, e⁻–h⁺ pairs are separated by an external electric field (e.g., \( V_{bias} = +2 \text{ V} \)), where the e⁻ and h⁺ are injected into the metal and nanotubes, respectively. At zero-bias voltage, the net current is zero due to the suppression of the photocurrent by e⁻ and h⁺ generation in the channel. Thus, the photocurrent in these devices requires a potential difference across the device channel. There is no decrease in the photocurrent with time in figure 6(b) as charge recombination and generation processes are equilibrated under a finite bias.

In the discussion of the time response of the device, a small \( \tau \) obtained in densely packed nanotubes is attributed to the transit response (\( \tau_t \)) of the carriers traveling across adjacent metal electrodes, the diffusion time (\( \tau_d \)) of the excess carriers, and the time constant (\( \tau_RC \)) set by the instruments, expressed as \( \tau = \sqrt{(2.2\tau_RC)^2 + \tau_t^2 + \tau_d^2} \) [47, 48]. In our measurement, \( \tau_RC \) and \( \tau_t \) were neglected in comparison to \( \tau \) since these showed nanosecond timescales. The main contribution of \( \tau \) in our densely-packed devices is described by the diffusion length (\( L_d \)) as \( L_d = \sqrt{KT/\mu} \) [33]. We calculated \( L_d \) from the measured \( \mu \) to be ~1 mm and
\(\sim 48 \mu m\) of Device B and F, respectively, by using \(\tau\) summarized in table 1. The larger \(L_d\) obtained in Device B implies a large carrier lifetime between photogeneration and recombination of charges, which is desired in photovoltaic-operation devices with no bias voltage. However, a short diffusion time is achieved in densely packed networks (Device F) since the increased number of nanotubes populates the scattering center for charge carriers that result in the reduction of \(L_d\).

The \(D^*\) of our assembled SWCNT photodetectors was determined using equation (3) with the NEP obtained by measuring the voltage noise spectral density \((S_V)\) on \(R_L\) in a specific frequency bandwidth \((\Delta f)\). In the noise measurement setup, we used \(R_L = 1 k\Omega\). Figure 7(a) shows the current noise spectral density \((S_n = S_V / R_L^2)\) of Device B, Device F, the instrument noise \((S_{inst} = 1.08 \times 10^{-23} A^2 Hz^{-1})\), and the thermal noise of \(R_L\) \((S_{th} = 4kT / R_L = 1.66 \times 10^{-23} A^2 Hz^{-1})\) in the frequency range of 10 kHz to 100 kHz. Here we consider our photodetectors as an electrical noise source under the influence of the external bias. For \(f < 60\) kHz, the 1/f noise of the devices was observed. The cut-off frequency was calculated as \(f_c = 1/(2\pi R_L C_P) \approx 1 MHz\) with \(C_P = 184\) pF (the capacitance per meter of RG-58 BNC cables and the input of the preamplifier \(\sim 20\) pF).

In the inset of figure 7(a), the \(S_1\) of Device F was measured at frequencies between 60 kHz and 99 kHz at two different light conditions. The two spectra show a small difference in the noise amplitude in comparison to laser ‘ON’ and ‘OFF’, which correspond to the histogram plots in figure 7(b). The data were taken below \(f_c \approx 1 MHz\) acquired at 751 points after root-mean-square (RMS) averaging of 100 times by the spectrum analyzer (SPA; Siglent 3021x). The resolution bandwidth (RBW) was set to 10 Hz. The bias resistance \((R_b = 2 M\Omega)\) was used to limit the current fed to the device (see the circuit diagram in figure 7(c)).

The histogram plot of Device F at laser “OFF” condition yields the peak at \(S_1 \approx 3.20 \times 10^{-23} A^2 Hz^{-1}\) that can be used to obtain the NEP of the device. Thus, by subtracting \(S_{inst}\) and \(S_{th}\), the actual value of \(S_1\) is \(\sim 4.55 \times 10^{-24} A^2 Hz^{-1}\), resulting in the current noise of \(\sqrt{S_1} \approx 2.13 pA Hz^{-1/2}\) generated from Device F. This noise level is much lower than the measured photocurrent \((I_p \approx 330 nA\), see figure 5(b)). Therefore, the NEP of Device F was found to be \(2.67 \times 10^{-7} W Hz^{-1/2}\). After normalizing with \(\sqrt{A}\), the maximum \(D^*\) was shown to be up to \(4.90 \times 10^5 cm Hz^{1/2} W^{-1}\), in Device F with the densely packed networks (table 1).

This value is comparable to some of the bolometers using suspended nanotube films [49, 50]. However, the devices studied here were pristine SWCNTs and so their detection performance can be further improved by incorporating other materials such as graphene, P3HT, polycarbonate, and fullerene (C60), etc., making nanocomposite networks for high-performance photodetectors [2, 51–53].

Our experimental results showed \(R_b, D^*, \text{ and } \tau\) values of up to \(8.0 \mu A W^{-1}, 4.9 \times 10^5 cm Hz^{1/2} W^{-1}\), and \(4\) ms, respectively, in the densely packed nanotube networks. This device had a higher gain than the device with a few nanotube depositions \((R_b, D^*, \text{ and } \tau = 1.1 nA W^{-1}, 6.1 \times 10^5 cm Hz^{1/2} W^{-1}\), and \(2.6\) s, respectively). These values are compared with the other SWCNT photodetectors, assembled with different techniques (table 2).

4. Conclusions

In conclusion, we have fabricated semiconducting nanotube (SWCNT) photodetectors using dielectrophoretic assembly with low and high work-function metals and studied the electronic properties of the random networks of the SWCNTs under the illumination of a near-infrared (NIR) laser. Our experimental results revealed the effect of Fermi-level pinning of bulk nanotube-metal contacts in the densely packed nanotube networks. After photoabsorption of the NIR laser, the devices showed photovoltaic (PV) and photoconductive (PC) characteristics. The detection performance of the devices determined by photoresponsivity, detectivity, and time response, strongly depends on photoabsorption area, channel resistance, and charge percolation in the random-nanotube networks. The device with densely pack nanotubes showed a photoresponsivity and detectivity of up to 4 orders of magnitude higher than that achieved in the device with a few nanotube depositions. The fast time response in the densely packed nanotube networks under a finite bias is attributed to the short-diffusion length of the photoexcited electrons and holes. The slow injection of electrons via diffusion results in the decrease of the photocurrent in the PV device with the low nanotube deposition. Our experimental investigations on the random networks of the nanotubes suggest a further study using \(1/f\) noise measurement to verify charge percolation in the nanotube networks with different channel geometries.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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