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Converting Ambipolar Double-Walled Nanotube Bundles to Unipolar Carbon Nanotube Field-Effect Transistor Devices by Inner Functionalization

George Chimowa, Emmanuel Flahaut, Venkateswara Rao Sodisetti, and Somnath Bhattacharyya*

Carbon nanotube (CNT)-based transistor devices have been demonstrated and are seen as the next-generation alternative to replace the current generation electronic devices based on silicon MOS technology. Their limitations, however, are related to their instability in ambient conditions and technical challenges in scaling up production of individual CNT devices. Herein, a simple technique to convert ambipolar (both n- and p-carrier) individual CNT-based transistors into unipolar (p-type carrier) transistors that carry large currents ≈±7 mA before saturation is demonstrated. Such large current-carrying capability from an individual or single-bundle CNTs will be ideal for applications that require high currents such as output stages of radio frequency (RF) and audio amplifiers. This work highlights the ability to tune CNT-based transistor devices to suit specific applications, which is essential for the development of next generation of nanoelectronics.

1. Introduction

Modern electronics has benefitted significantly from scaling down the channel length of metal–oxide–semiconductor field-effect transistors (MOSFET) from microscale into the nanoscale regime. This has enabled the packaging of thousands of transistors into small microprocessors almost the size of one's thumbnail, which consumes low energy and has low operating voltages. However, challenges arise due to short channels, such as high leakage currents because of quantum tunneling,[1] drain-induced barrier lowering (DIBL),[2] and the Fermi–Dirac-limited subthreshold (SS) swing of the metal–oxide–semiconductor (MOS) technology.[3] New materials for transistor manufacturing are therefore required if the scaling down of device size is to be continued further beyond 30 nm. Silicon tunneling field-effect transistors have shown promising fast switching, but their limiting factor is the high bandgap of the material.[4]

It is against this background that carbon nanotubes (CNTs) have emerged as potential transistor devices due to their nanoscale dimension, excellent electrical properties, which include high current mobility, and low bandgap (0.6–0.8 eV) which depends on their diameters and chirality.[5–7] Semiconducting double-walled nanotubes (DWNTs) exhibit both p-type and n-type (ambipolar) characteristics which are not so much observed with single-walled nanotubes (SWNTs).[8] This ambipolar behavior of DWNT devices makes them ideal for light-emitting transistors as the holes and electrons recombine to emit a photon. There are however other applications which require unipolar devices such as fast switching transistors for high-frequency applications. It is therefore essential that ambipolar devices be made into stable unipolar devices.

Another limiting factor of the semiconducting SWNT transistor devices that have been reported so far is the low ON current normally in the nano-Ampere (nA) range.[9–11] Such low currents will not be sufficient for the output stages of sound amplifiers and some radio frequency (RF) output amplifiers that require high currents to produce enough energy to vibrate the speaker diaphragm or power the antennas of telecommunications devices. In this light, individual CNT bundles or DWNTs capable of carrying higher currents will be ideal for these applications. The DWNT individual bundle transistor devices reported in this article show great promise in this aspect as they can carry current in the mA regime in agreement with previous predictions for large-diameter DWNTs with low array density, which is not observed in SWNTs.[12]

Often SWNT-based transistors' performance is influenced significantly by the ambient air as it makes the SWNT into p-type doped material,[13] such behavior is not ideal for stable and reliable devices. Unlike SWNTs, DWNTs have also been reported to

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have better SS = inverse $\left(d\log\frac{I_d}{dV_{gs}}\right)$.[14] It is against this background that this work sought to find ways of making high-current DWNT-based transistors and explore the important parameters such the transconductance (g_m), SS, and I_{on}/I_{off} current ratio. The operation of these transistors was also investigated at liquid nitrogen temperatures, and it was shown that the overall device performance improves, highlighting the significance of suppressing thermal processes. Such fundamental studies are important as they set a framework for innovative ideas in future application.

Using inner functionalization of DWNTs, a technique not commonly used, ambipolar pristine DWNTs can be converted into unipolar (p-type) transistors that are stable. Similar attempts were made with graphene field-effect transistors in which titanium was deposited on the graphene surface-induced p-type doping.[15] While there are several chemicals techniques that can be applied to induce p-type doping of carbon-based materials, inner functionalization has added advantages. Namely, inner functionalization retains the CNT's 1D property, as the outer surface area is not altered and second the density of states is improved as was shown previously.[16] So, to some extent, the important fundamental properties of CNTs are preserved and some properties such as sensitivity to gases are improved as the outer surface area is not affected.

The current work reported here lays a strong foundation for high-current DWNT-based unipolar transistor devices that can be used in applications which require relatively high currents such as the ones mentioned earlier.

2. Experimental Section

DWNTs were synthesized using a chemical vapor deposition technique as outlined in the article Communication.[17] The DWNTs were then opened at their ends by mixing 1 g of DWNTs, with 3.5 mL distilled water and 25 mL of 37% HCL and sonicated for 20 min. The solution was filtered and neutralized using 1.5 L of distilled water. DWNTS were then heated at 400 °C for 30 mins followed by heating in vacuum at 200 °C for 4 h to ensure maximum drying. The inner functionalization with ZnI_2 was done as outlined in the article.[18] The mixture was then washed with warm ethanol several times to remove the excess of ZnI_2 outside the nanotubes and ensured that all remaining ZnI_2 was present as filling inside the nanotubes.

The inner functionalized DWNTs were then examined by transmission electron microscopy to check the success of the filling. Transmission electron microscopy (TEM) images are shown in Results. After this, the functionalized DWNTs were made into back-gated transistor devices by aligning individual bundles using the dielectrophoresis method on prefabricated electrodes, whose structure dimensions are shown in **Figure 1**a,b. Figure 1a shows the electrode top layout and Figure 1b shows the cross-sectional view. The back side was heavily p-doped silicon, which was used as the gate terminal, while two of the top electrodes were used as source and drain depending on which terminals the DWNTS were aligned (either the inner or outer electrodes). To ensure that we investigated DWNTs of almost the same length, devices on which DWNTs were aligned across the

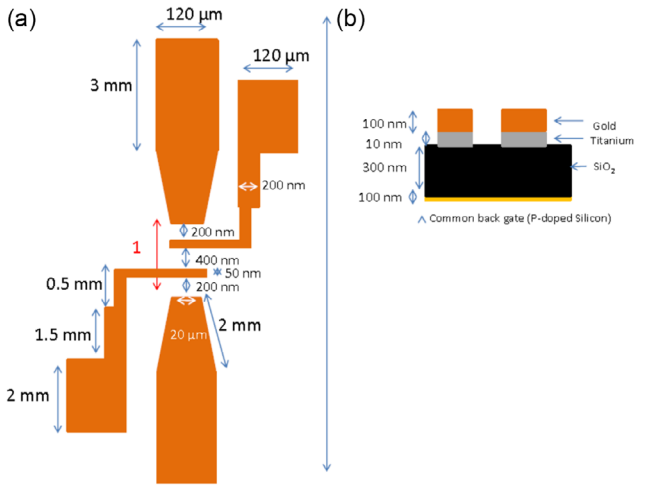

Figure 1. a) Top view of electrode layout for the transistor devices. b) Cross-sectional view shows that a common back gate is below the top gold source and drain terminals.

1 µm gap (outer electrodes) were chosen for this investigation; see field-emission (FE) scanning electron microscopy (SEM) images in Figure 3.

The transistor characteristics were measured using the Agilent semiconductor parameter analyzer system B 1500 A. The Instrument was attached to a Janis Cryogenic system, which enabled low-temperature measurements, performed by flowing liquid nitrogen through an evacuated system.

3. Results and Discussions

As aforementioned, the filled/inner-functionalized DWNTs were analyzed using a high-resolution transmission electron microscope (HRTEM) in both bright- and dark-field modes, to check the effectiveness of filling.

From the HRTEM dark-field images in **Figure 2**, it is evident that the filling method used in this work was effective, with some CNTs even getting filled over the entire 30–40 nm nanotube length see Figure 2a. Figure 2c,d shows energy dispersive X-ray analysis (EDX) spectra of the filled nanotube, confirming that the filling material is a composition of zinc, iodine, and/or zinc iodide.

After material characterization, the filled DWNTs were made into back-gated transistors on the prefabricated devices as mentioned earlier. The FESEM images in **Figure 3** show an illustration of some of the devices.

The scanning electron microscopy images show individual bundles of DWNTs aligned across the source and drain contacts. No additional top metal was evaporated to improve the contacts, resulting in most likely Schottky barrier contacts, and this has a significant effect on the device performance which shall be explained later.

Figure 4a,b shows the output characteristics of the CNT transistor device made from pristine DWNTs bundles. What is significant is the high current that the device can carry, maximum of 8 mA at 77 K and about 6 mA at 295 K for $V_{ds} = 2$ V and $V_{gs} = -1$ V. This is in accordance with the extensive numerical study by Huang et al., who predicted large on currents, when the

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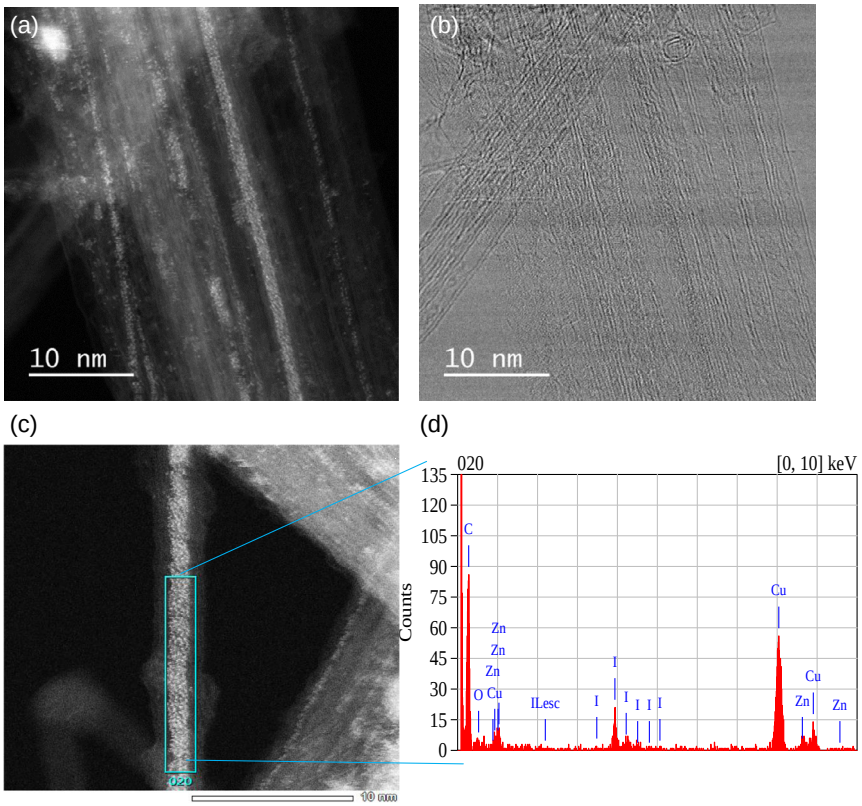

Figure 2. a) Dark-field HRTEM image of the filled DWNTs, some CNTs showing filling over the entire shown area. b) Bright-field HRTEM image of the image shown in (a), showing the double walls of the CNTs. c) Dark-field HRTEM image showing one filled individual CNT. d) EDX spectra on the segment of the CNT in (c), showing the presence of zinc, iodine, and copper from the sample holder.

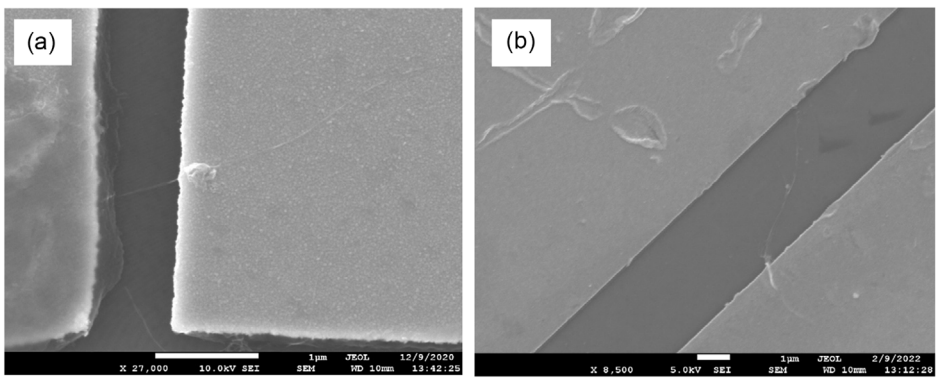

Figure 3. FESEM images of the individual DWNT bundles deposited on gold contacts which make the source and drain contacts in the transistor devices. a) Device made from pristine DWNTS. b) Device made from ZnI-filled DWNTs.

DWNT diameters are large and the array density is low.[12] The current begins to get significantly pinched only when the gate voltage is above 2 V for measurements done at 295 K, see Figure 4a. This is an indication that the gate oxide layer is too thick at 300 nm. Reducing this oxide layer thickness will predictably lower this gate voltage. It is also observed that lowering the device temperature to 77 K, Figure 4b, results in enhanced electron current pinching effect when compared to the case when temperature is 295 K.

When zinc iodide (ZnI)-filled/inner-functionalized DWNTs were measured, the output characteristics in **Figure 5** show different behavior from that of pristine DWNTs. The filled DWNTs (Figure 5a) show that the hole current gets pinched significantly when the gate voltage is above zero (0 V). It is also observed that the maximum electron current is almost 10 times larger than for pristine DWNTs. Lowering the temperature (Figure 5b) to 76 K has the same effect as before, which is to increase the maximum overall current (i.e., it increases from 25 to 35 mA when

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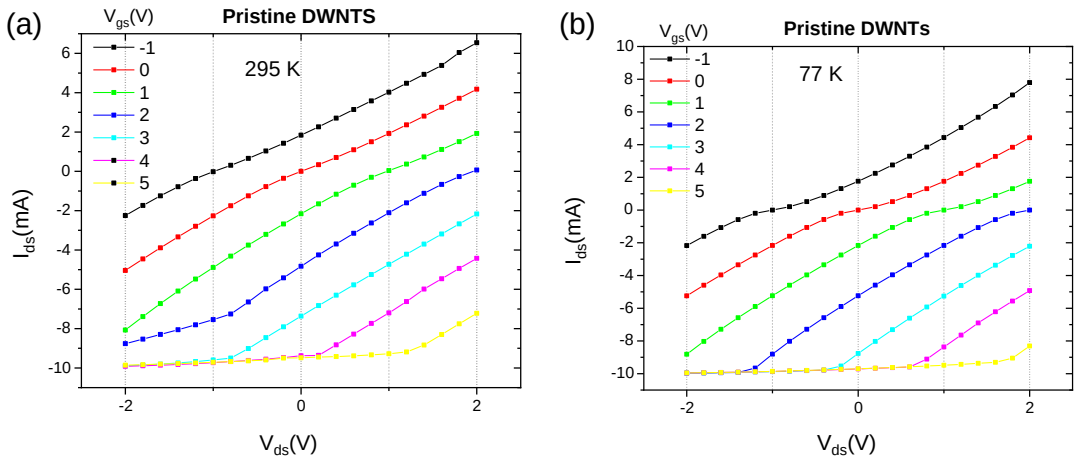

Figure 4. a) Output characteristics of pristine DWNTs devices at 295 K as the gate voltage was varied from −1 to 5 V. b) Output characteristic of the same device at 77 K, with the gate voltage being varied from −1 to 5 V.

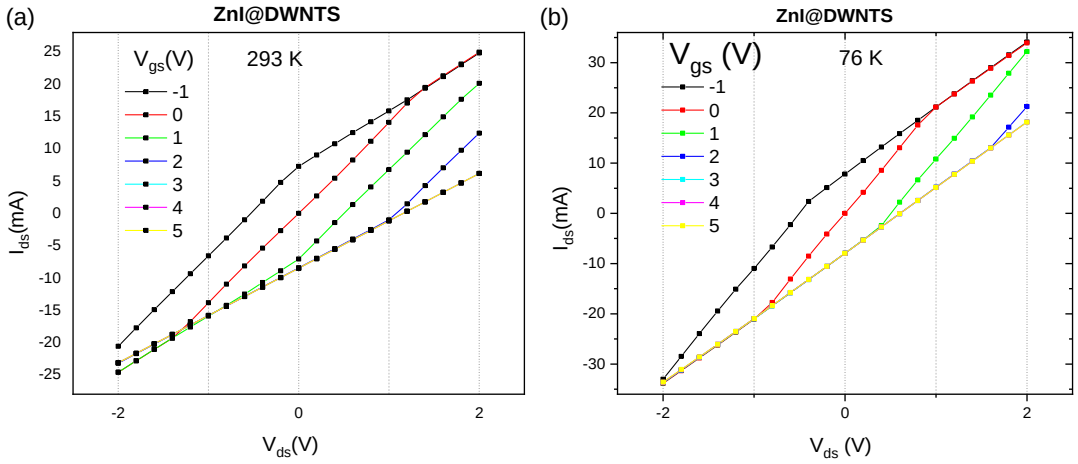

Figure 5. a) Output characteristics of ZnI-filled DWNT devices at 293 K as the gate voltage was varied from −1 to 5 V. b) Output characteristic of the same device at 76 K, with the gate voltage being varied from −1 to 5 V.

$V_{ds} = 2$ V at $V_{gs} = 0$ V). Such high currents to the best of our knowledge have not been observed in CNT transistor devices made of individual bundles; only CNT networks have been shown to have such high currents.[19]

The device transfer characteristics of the two transistors shown in **Figure 6** clearly show the unique differences between the two types of DWNT devices. The pristine DWNTs device, Figure 6a, demonstrates ambipolar transport, with hole current dominating when V_{gs} is negative and electron current dominates for positive V_{gs} values. The transition between the two types of transport occurs when $V_{gs} = V_{ds}$. DWNTs filled with zinc iodide, Figure 6b, show that the electron current gets suppressed, indicating that the DWNTs are p-doped. This agrees with other previous studies which have shown that iodine causes p-doping of CNTs.[20]

While this work has demonstrated large-current CNT transistor devices, they can be manipulated from ambipolar to unipolar devices, and it is evident that the switching capabilities are still very poor. The SS for hole current in the pristine device is about 2.3 V dec^{-1} and for the filled DWNTs is about 4.8 V dec^{-1}, which are very far from a target of less than 60 mV dec^{-1}. This might not be surprising because the gate oxide is about 300 nm, meaning that gate voltage effect on the charge carrier transport in the CNT channel device is weak. Furthermore, the devices are typical Schottky barrier devices as the CNTs were just placed on top of the electrodes, making poor van der Waals contacts with the source–drain electrodes. The I_{on}/I_{off} current ratio for pristine DWNT devices is $\approx 10^3$ A for the electron current, which is 10^2 lower than the ideal value, demonstrating high leakage currents and hence there is need to further improve device physical geometry. The filled DWNTs devices have even lower I_{on}/I_{off} current ratio.

The transconductance (g_m) for the hole current for both devices is not very different, −2.5 mS for the pristine and −2.2 mS for the filled DWNTs. What is evident is that for the filled DWNTs the transconductance has some temperature dependence (−3.2 mS at 76 K and −2.2 mS at 295 K), which is not the case with pristine DWNTs. A closer look at Figure 6b shows

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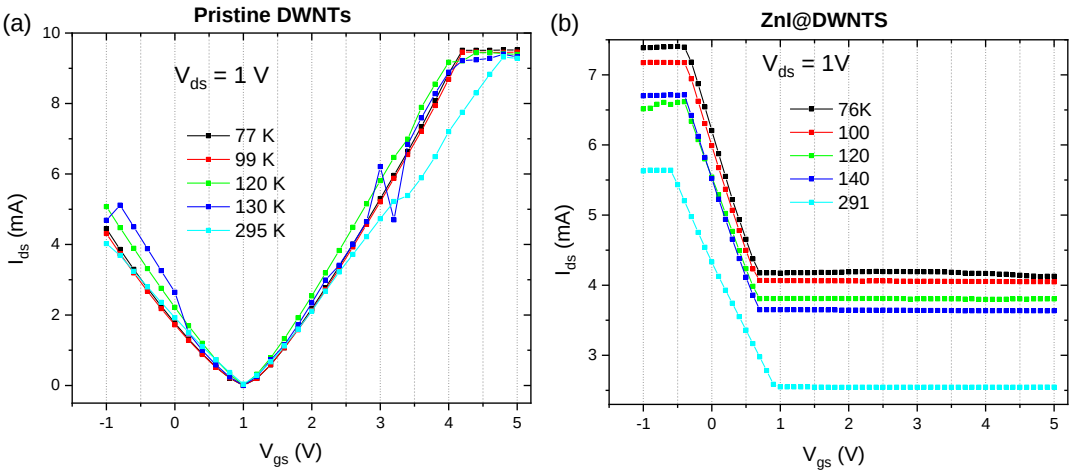

Figure 6. a) Transfer characteristics of the pristine DWNTs showing ambipolar transport. b) Transfer characteristics of zinc iodide-filled/functionalized DWNTs, showing that electron current is suppressed.

that the hole current saturates at −0.5 V, suggesting a limited hole carrier concentration. To understand the earlier discussed observations, we proposed a simple band diagram shown in **Figure 7**.

In the schematic diagram in Figure 7, for pristine DWNTs, the carriers' (holes or electrons) Fermi levels are close to the chemical potential ($\mu_s$and μ_D)of the contact electrodes. The source–drain bias voltage (V_{ds}) will result in a slight tilting of the CNT energy band towards the drain terminal, and the chemical potential at the drain will be pushed down by energy equal to $qV_{ds,}$ where q is the charge on an electron. The varying gate voltage modulates both the Schottky barrier potentials at the contacts and the positions of the carrier Fermi level, since it is over the entire length of CNT device including the contacts. When V_{gs} is positive, electron current dominates, and the reverse is true when V_{gs} is negative, that is, hole current dominates.

The effect of zinc iodide filling is that the CNT gets p-doped; this pushes the hole Fermi level up toward the middle of the CNT bandgap. At this position, modulating potentials due to the bias voltage and the gate voltage results in the observed pronounced hole current and suppressed electron current. ZnI filling of DWNTs does not only result in p-doping but appears to increase the current-carrying capacity of the CNTs, which might be because of the increased density of states due to the encapsulated material.[16] The surprising aspect is the limited hole current which saturates above −0.5 V. A possible reason might be the Schottky barrier contacts that might result in a higher energy gap between the source chemical potential (μ_s) and the hole Fermi level (E_{fh}), since the whole energy gets tilted toward the left (source terminal) during the hole current flow. The low I_{on}/I_{off} current ratio and the large value of SS require improvements in the device architecture such as reducing the back oxide layer thickness and introducing top gates that allow local modulation to the channel.

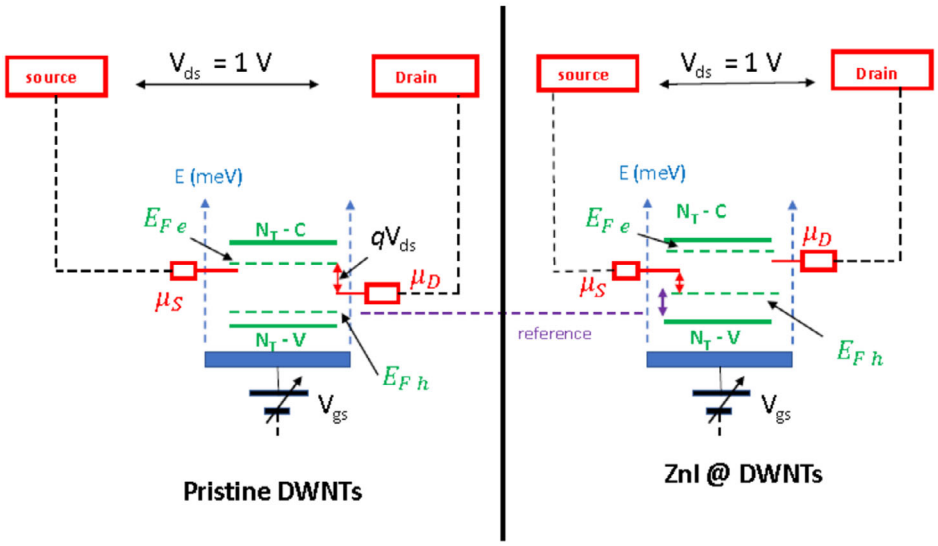

Figure 7. A schematic illustration of the band diagram for both the pristine DWNTs and ZnI-filled DWNTs.

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4. Conclusion

Despite the nonideal I_{on}/I_{off} current ratio and the large value of SS, this work has demonstrated high-current-carrying CNT transistors made from individual DWNTs. Inner functionalization or encapsulating of zinc iodide inside the CNTs results in p -doping and in so doing suppressing the electron current. The inner functionalization preserves the integrity of the outer CNT wall, which is not possible with other p-doping techniques. This technique makes ambipolar devices into unipolar devices. This achievement lays a strong foundation for CNT-based transistors that can be used in fields requiring high currents such as power amplifiers and RF output stages of electronic transmission equipment that power antennas. Improvement of the device architecture will enhance some of the poor observed parameters.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

endohedral filling, functionalization, nanoelectronics, nanowires

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