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# Converting Ambipolar Double Walled Nanotube bundles to Unipolar Carbon Nanotube Field Effect Transistor devices by inner functionalization

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**Keywords:** nanoelectronics, functionalisation, endohedral filling, nanowires

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## Abstract:

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. This work demonstrates a simple technique to convert ambipolar (both  $n$  &  $p$ -carrier) individual CNT based transistors into unipolar ( $p$ -type carrier) transistors that carry large currents approximately  $\pm 7$  mA before saturation. Such large current carrying capability from an individual or a single bundle CNTs will be ideal for applications that require high currents such as output stages of radio frequency (RF) and audio amplifiers. Our 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.

## Introduction

Morden electronics has benefitted significantly from the scaling down the channel length of metal oxide semiconductor field effect transistors (MOSFET) from micro scale into the nano-scale regime. This has enabled the packaging of thousands of transistors into small microprocessors almost the size of one's thumb nail, that consume low energy and have low operating voltages. However, challenges, arise due to short channels, such as high leakage currents because of quantum tunnelling [1], Drain induced Barrier lowering (DIBL) [2] and the Fermi - Dirac limited sub threshold

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(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 tunnelling 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 have emerged as potential transistor devices due to their nano-scale dimension, excellent electrical properties, which include high current mobility, and low bandgap (0.6 – 0.8 eV) which depends on their diameters and chirality [5,6,7]. Semiconducting double walled nanotubes (DWNTs) exhibit both *p*-type and *n*-type (ambipolar) characteristics which is not so much observed with single walled nanotubes (SWNTs) [8]. This ambipolar behaviour of DWNTs 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 SWNTs transistor devices that have been reported so far, is the low ON currents normally in the nano-ampere (nA) range [9,10, 11,]. Such low currents will not be sufficient for the output stages of sound amplifiers and some RF output amplifiers that require high currents to produce enough energy to vibrate speaker diaphragm or power the antennas of telecommunications devices. In this light, individual CNT bundles or double walled nanotubes 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 behaviour is not ideal for stable and reliable devices. Unlike SWNTs, DWNTs have also been reported to have better sub threshold swing (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 ( $g_m$ ), sub-threshold swing, and the  $I_{on} / I_{off}$  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.

By 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 deposition 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 functionalisation has added advantages. Namely, inner functionalization retains the CNT's one dimensionality property, as the outer surface area is not altered and secondly 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 is improved as the outer surface area is not affected.

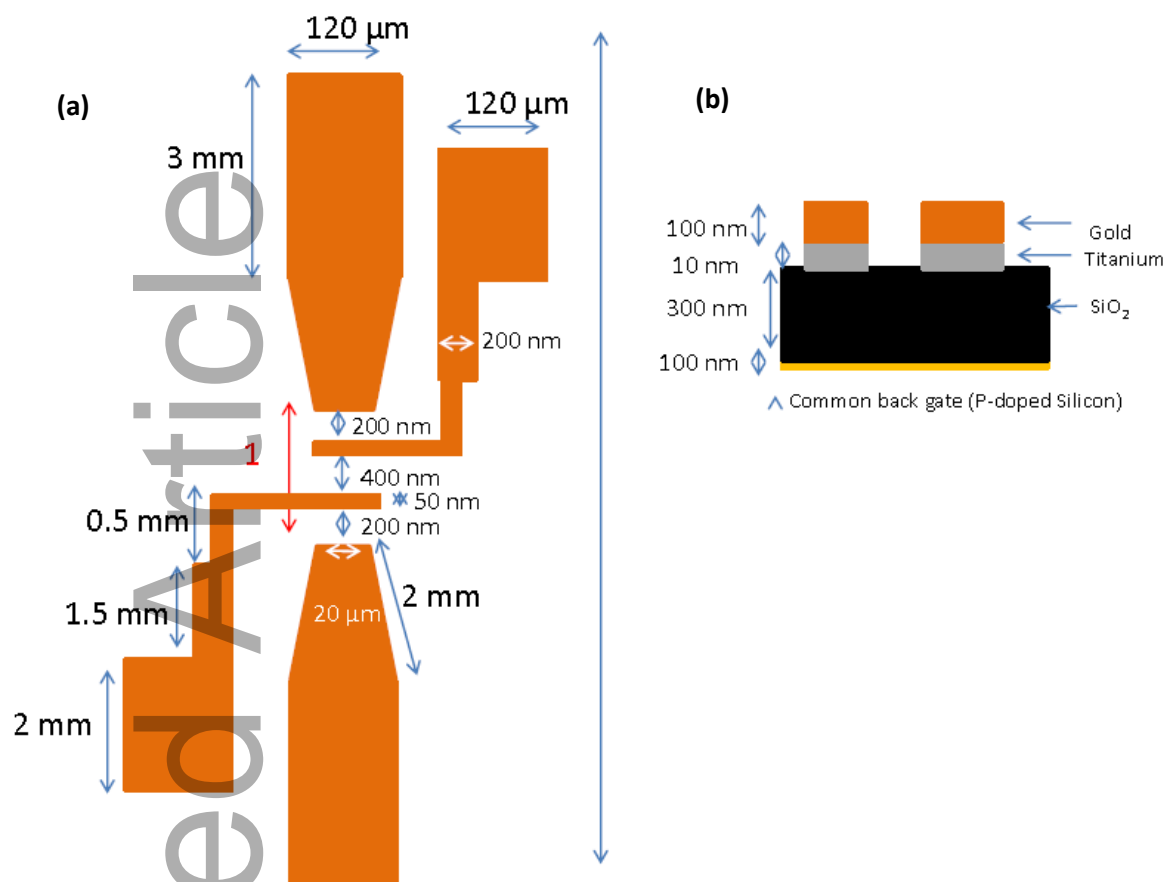
The current work reported here, lays a strong foundation for high current DWNT based unipolar transistor devices that can be used in applications which require relatively high currents such as the ones mentioned earlier.

### Methodology

Double walled carbon nanotubes were synthesized using a chemical vapour 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 minutes. The solution was filtered and neutralized using 1.5 L of distilled water. The DWNTS were then heated at 400°C for 30 mins followed by another heating in a vacuum at 200°C for 4 hours to ensure maximum drying. The inner functionalization with ZnI<sub>2</sub> was done as outlined in the article [18]. The mixture was then washed with warm ethanol several times to remove the excess of ZnI<sub>2</sub> outside the nanotubes and ensure that all remaining ZnI<sub>2</sub> was present as filling inside the nanotubes.

The inner functionalized DWNTs were then taken for transmission electron microscopy to check the success of the filling, TEM images are shown in the results section. After this, the functionalized DWNTs were made into back gated transistor devices by aligning individual bundles using dielectrophoresis method on prefabricated electrodes whose structure dimensions are shown in Fig.1 (a & b). The figure 1 (a) shows the electrode top layout and figure 1(b) shows the cross-sectional view. The back side is 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 will be 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 1-micron gap (outer electrodes) were chosen for this investigation see field emission (FE)-SEM images in Figure 3.

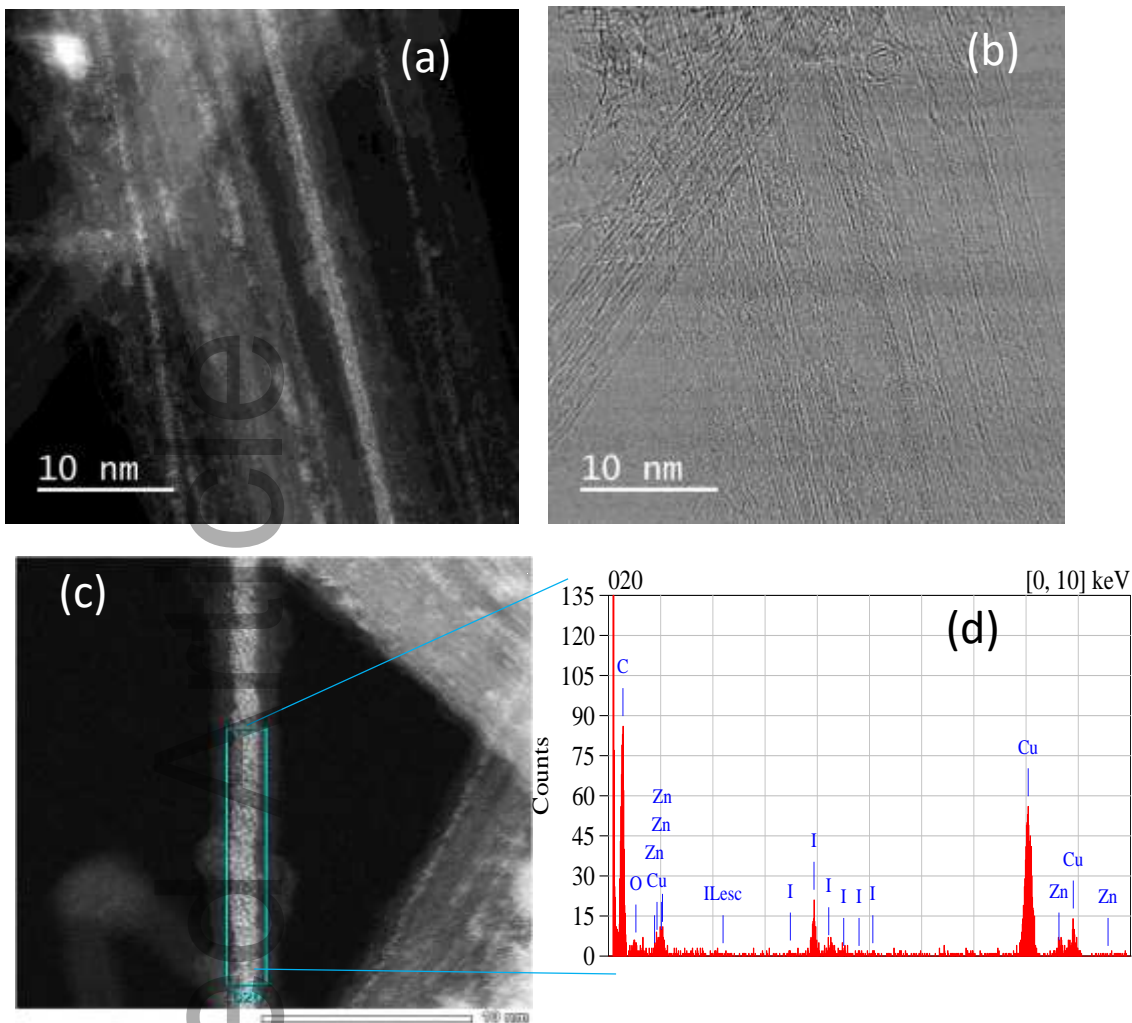


**Fig. 1:** (a) Top-view of electrode layout for the transistor devices (b) Cross-sectional view showing that a common back gated is below the top gold source and Drain terminals.

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

## Results and Discussions

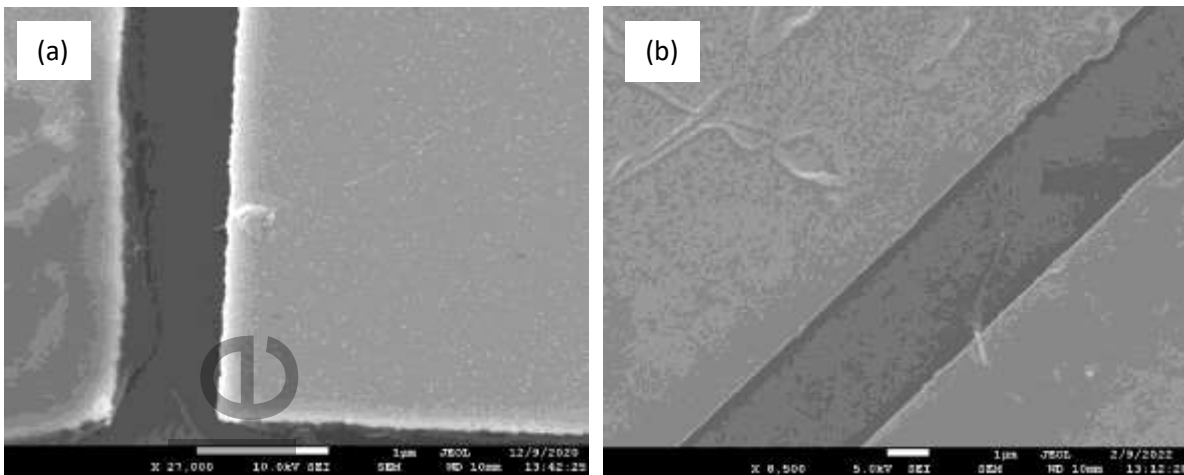
As aforementioned the filled /inner functionalised DWNTs were analysed using high resolution transmission electron microscope (HRTEM) in both bright and dark field modes, to check the effectiveness of the filling.



**Fig. 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 taken on the segment of the CNT in (c), showing the presence of Zinc, Iodine and Copper from the sample holder.

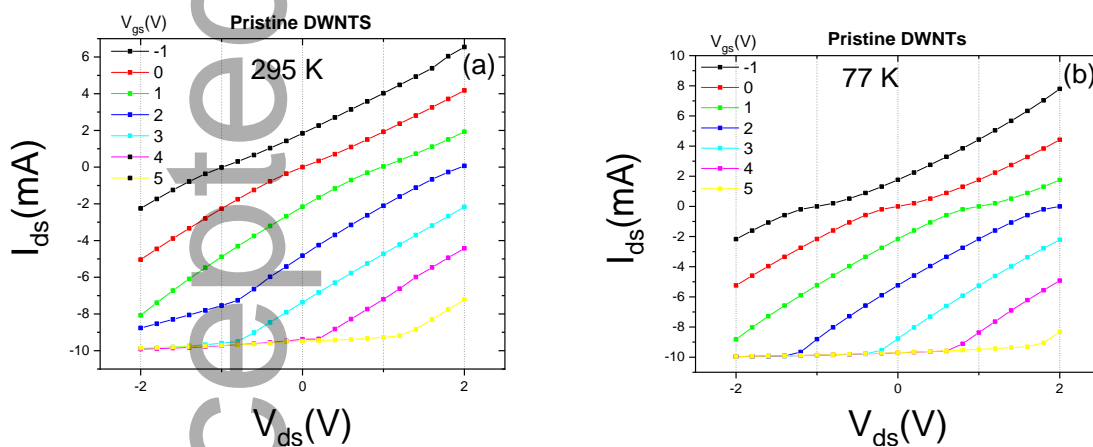
From the HRTEM dark field images in Figure 2, it is evident that the filling method used in this work was effective, with some CNTs even getting filled over the entire 30 to 40 nm nanotube length see Fig. 2 (a). Figure 2 (c and d) shows EDX spectra of the filled nanotube confirming that the filling material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

After material characterisation, the filled DWNTs were made into back gated transistor on the prefabricated devices as mentioned earlier. The FE- SEM images in Fig.3 shows an illustration of some of the devices.



**Fig.3:** FE- SEM images of the individual DWNT bundles deposited on gold contacts which make the source and drain contacts making the transistor devices, (a) Device made from pristine DWNTs, (b) Device made from ZnI filled DWNTs.

The scanning electron microscopy images shows 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.

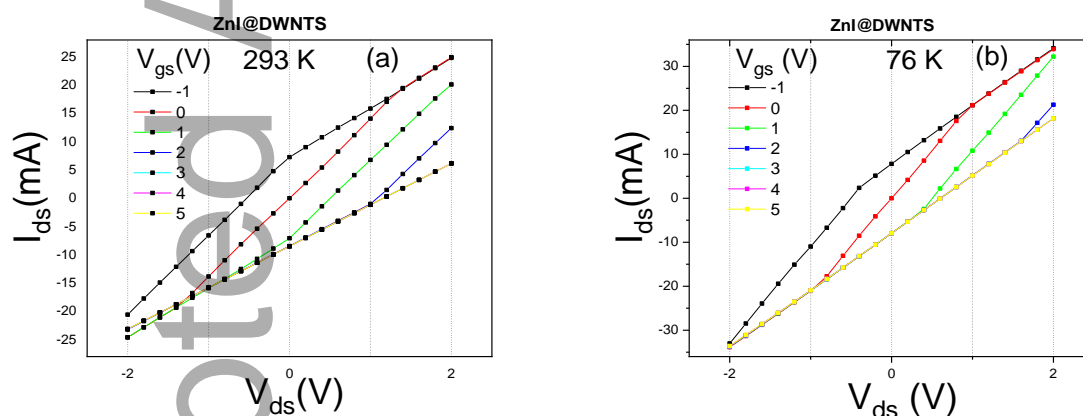


**Fig. 4:** (a) Output characteristics of Pristine DWNTs devices at 295 K as the gate voltage was varied from -1 to 5 V. (b) Output characteristic of the same device at 77 K, with the gate voltage being varied from -1 to 5 V.

Figure 4 (a and 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 J. Zh. Huang et. al., which predicted large on currents, when the 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 Fig. 4 (a), 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, Fig.4 (b), results in enhanced electron current pinching effect when compared to the case when temperature is 295 K.

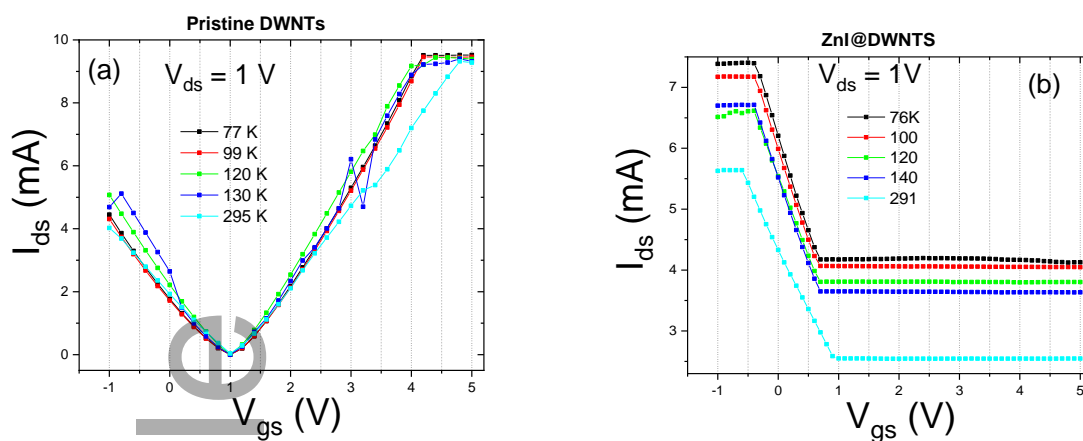
When the zinc iodide (ZnI) filled /inner functionalised DWNTs were measured. The output characteristics in Figure 5, shows different behaviour from that of Pristine DWNTs. The filled DWNTs, (Fig.5(a)), shows that the hole current gets pinched significantly when the gate voltage is above zero (0 V). It is also observed that the maximum electron current is almost 10 times larger than for pristine DWNTs. Lowering the temperature, (Fig.5 (b)), to 76 K has the same effect as before, which is to increase the maximum overall current (i.e., it increases from 25 mA to 35 mA when  $V_{ds} = 2$  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].



**Fig. 5:** (a) Output characteristics of ZnI filled DWNTs 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.

The device transfer characteristics of the two-transistor shown in Figure 6, clearly show the unique differences between the two types of DWNT devices. The pristine DWNTs device, Fig.6 (a), 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  $V_{gs} = V_{ds}$ . The DWNTs filled with Zinc Iodide, Fig. 6 (b), shows that the electron current gets suppressed, indicating that the DWNTs have become  $p$  doped. This agrees with other previous studies which have shown that Iodine, causes  $p$ -doping of CNTs [20].





**Fig. 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.

While this work has demonstrated, large current CNT transistor devices, that can be manipulated from ambipolar to unipolar devices, it is evident that the switching capabilities are still very poor. The sub threshold swing (SS) for the hole current in the pristine device is about 2.3 V/dec and for the filled DWNTs is about 4.8 V/dec, which are very far from a target of less than 60 mV/dec. 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  $\sim 10^3$  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 are 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 Fig.6 (b), shows that the hole current saturates at - 0.5 V, suggesting a limited hole carrier concentration. To understand the above discussed observations, we proposed a simple band diagram shown in Fig.7.

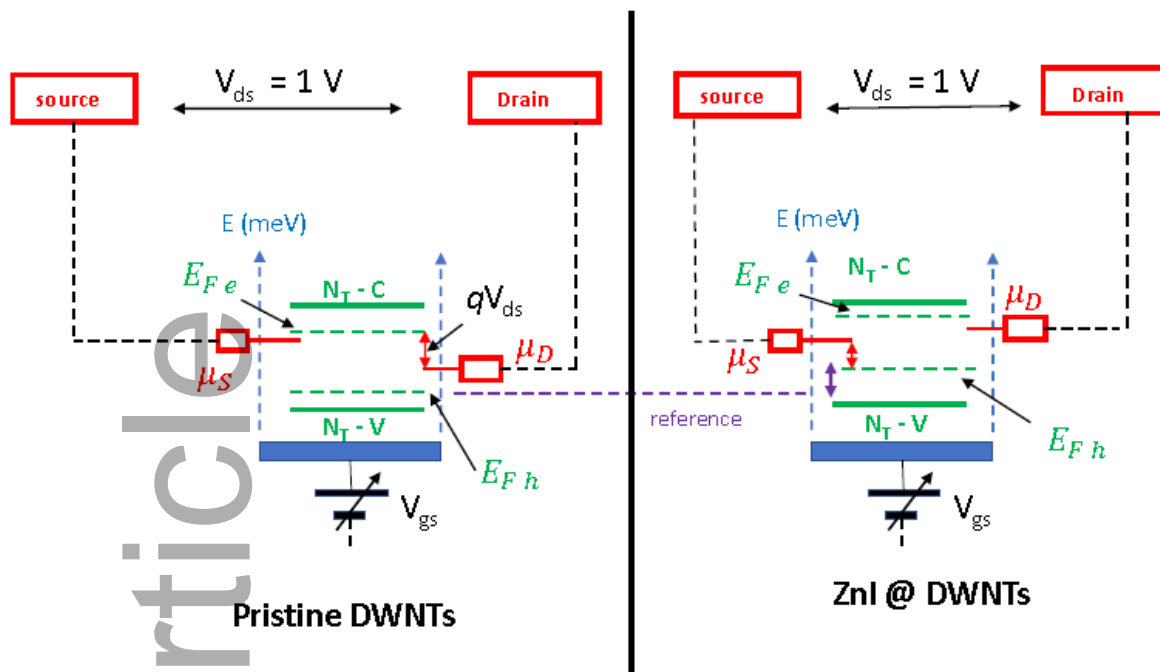


Fig. 7: A schematic illustration of the band diagram for both the pristine DWNTs and ZnI filled DWNTs.

In the schematic diagram in Fig. 7, for pristine DWNTs, the carriers (holes or electrons) Fermi levels are close to the chemical potential ( $\mu_S$  and  $\mu_D$ ) 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 as well 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, i.e., hole current dominates.

The effect of the zinc iodide filling is that the CNT gets  $p$ -doped, this pushes the hole Fermi level up towards the middle of the CNT band gap. 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. The ZnI filling of the DWNTs does not only result in the  $p$ -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 ( $\mu_S$ ) and the hole Fermi level ( $E_{f h}$ ), since the whole energy gets tilted towards the left (source terminal) during the hole current flow. The low  $I_{on} / I_{off}$  current ratio and the large value of SS, requires improvements in the device

architecture such as reducing the back oxide layer thickness and introducing top gates that allow local modulation to the channel.

## Conclusions

Despite the non-ideal  $I_{on} / I_{off}$  current ratio and the large value of  $SS$ , this work has demonstrated high current carrying CNTs transistors made from individual double walled carbon nanotubes. Inner functionalisation or encapsulating of Zinc iodide inside the CNTs results in  $p$ -doping, and in so doing suppressing the electron current. The inner functionalisation 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 improve some of the poor observed parameters.

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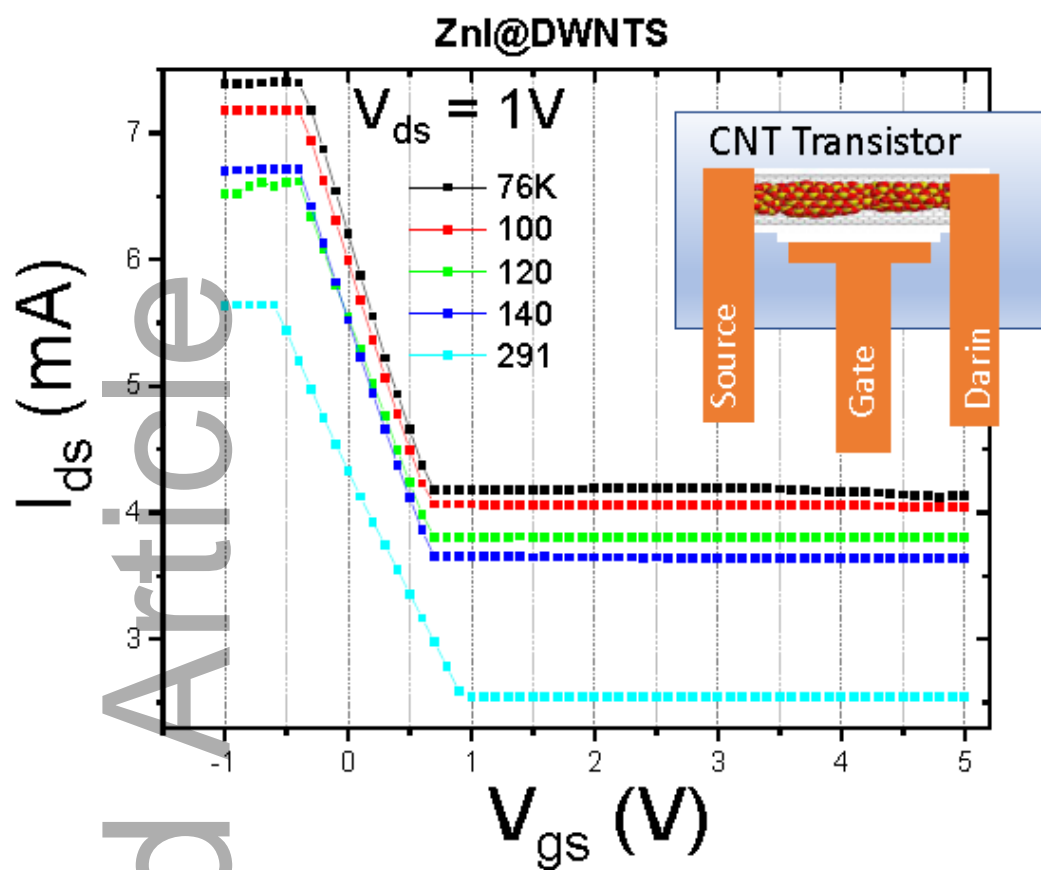
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## TOC Text

CNT transistors devices are seen as the next generation fast switching and energy efficient nanodevices. This work demonstrates a big step towards this noble goal by showing practical unipolar CNT transistors with high current carrying capacity than has been done before using individual double walled carbon nanotubes. Such large currents are needed for the output stages for some electronic devices.



**TOC Fig:** Transfer characteristics of filled double walled carbon nanotubes demonstrating unipolar behaviour of Zinc iodide filled CNTs. Inset: Schematic model of a CNT transistor.