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An ultra-low leakage current single carbon nanotube diode with split-gate and asymmetric contact geometry

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A single carbon nanotube diode is reported, with Ti and Pd contacts, and split gates. Without gate bias the device displays strong rectification, with a leakage current (I_0) of 6×10^{-16} A, and an ideality factor (η) of 1.38. When the gate above the Ti contact is biased negatively the diode inverts. When positive bias is then applied to the gate above the Pd contact minority carrier injection is suppressed. Configured such I_0 and η were 2×10^{-14} A and 2.01, respectively. Electrical characterization indicates that the Schottky barrier height for electrons is lower for the Pd contact than the Ti contact. © 2013 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4823602>]

Carbon nanotube (CNT) based semiconductor devices offer significant potential advantages over traditional Si based technology including the highest reported mobility of any semiconductor¹ and nanometre (nm) scale geometries. The diode is a fundamental building block of most semiconductor based electronics. Various methods of forming p-n junctions have been used to demonstrate diode-like behaviour in CNT devices including coating one side of the channel with a polymer,² doping one side of the channel with donors,³ intramolecular “Y” junctions⁴ and kinks,⁵ intermolecular (CNT crossover) junctions,⁶ and split gates (a separate gate for the source and drain ends of the channel).^{7,8} Of these device geometries, split gates are arguably the most promising since they can display ideal diode behaviour and low leakage currents,⁹ efficient electroluminescence,¹⁰ and large photocurrents.¹¹ Diode-like behaviour has also been demonstrated using asymmetric contacts^{12–17} where the source and drain contacts are different metals. In this work we report a CNT diode having both asymmetric contacts and split gates. With no bias applied to the gates the device behaves as a Schottky diode with extremely low leakage current. The diode can be inverted by applying opposite bias to the split gates. Such very low leakage diodes may have applications in the power supply for mobile communication devices where they could increase standby time.¹⁸ On the other hand, the ability to invert the rectification direction of the diode could have applications in high speed signal processing.¹⁹

Devices were fabricated by growing single walled nanotubes (SWNTs) on a SiO₂/Si wafer by ethanol chemical vapour deposition with 0.1 nm of Co catalyst patterned using photolithography. Electron beam (EB) lithography was used to pattern source and drain contacts which were deposited by EB evaporation of 30 nm of Pd or Ti, respectively. A gate insulator was formed by atomic layer deposition (ALD) of 40 nm of Al₂O₃, following which split gates (gates 1 and 2) were fabricated by EB lithography and deposition of Ti/Au. Current-voltage (IV) scans were obtained using a Keithley

4200 SCS incorporating remote preamplifiers. A tungsten probe was directly connected to a remote preamplifier via 1 cm of triaxial cable. The preamplifier was then attached to a probe station along with three standard probes, with the measurements undertaken within a Faraday cage. The highest current resolution (~ 500 aA) was found to occur when the probe station and Faraday cage were biased to the shield and earth potentials, respectively. SEM images were taken using a Zeiss Evo50 at 2 kV using in-line lenses.

Pd has a high work function of 5.12 eV and is widely reported to make an ohmic contact with the valence band of CNTs.²⁰ In contrast, Ti has an intermediate work function of 4.33 eV which is approximately aligned with the middle of the CNT bandgap and able to form a Schottky barrier at the Ti/CNTs interface.¹⁷ Figure 1(b) shows an image of a single CNT bridging the channel. As the CNT is encapsulated beneath 40 nm of Al₂O₃ it is unlikely that the image is derived purely from secondary electrons; we propose that the contrast mechanism observed in the image results from charge build up in the nanotube and its metal contacts, leading to enhanced secondary electron yield directly above the CNT. A similar contrast mechanism is thought to occur with bare CNTs on insulating substrates.²¹

Figure 2 shows the IV characteristics of the CNT diode at various split gate biases. With no gate bias, the device displays strong rectification with a reverse bias leakage current below the resolution of the detection system (~ 500 aA). Applying a negative and positive bias to gates 1 and 2, respectively, caused inversion of the diode, but with a higher leakage current observed. Applying a negative and zero bias to gates 1 and 2, respectively, also caused inversion of the diode but with an even higher leakage current than with opposite split gate bias. Applying positive and negative bias to gates 1 and 2, respectively, or a bias to gate 2 alone (not shown) resulted in higher leakage currents and no inversion. To extract diode parameters the IV curves can be analysed using the diode equation,

$$I = I_0 \left[\exp \left(\frac{V - IR_s}{\eta V_T} \right) - 1 \right], \quad (1)$$

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FIG. 1. (a) Schematic cross-section of the device structure. The split gate separation was $2\ \mu\text{m}$ and the source/drain to gate separation was $1\ \mu\text{m}$, giving a total channel length of $3\ \mu\text{m}$. (b) SEM image of the device, only one CNT was observed bridging the channel.

where I_0 is the leakage current, R_s is the series resistance, η is the diode ideality factor, and V_T is the thermal voltage $= kT/q$, where k is the Boltzmann constant and q is the elementary charge. There is no analytical solution to Eq. (1) using standard mathematical functions, and approximate graphical methods are often used to extract I_0 , R_s , and η . However, Eq. (1) can be expressed as a transcendental equation of the form $we^w = x$, the solution of this is the multi-valued Lambert W-function. An explicit solution to Eq. (1) is given as follows:²²

$$I = \frac{\eta V_T}{R_s} W_0 \left[\frac{I_0 R_s}{\eta V_T} \exp \left(\frac{V + I_0 R_s}{\eta V_T} \right) \right] - I_0, \quad (2)$$

where W_0 is the real positive branch of the Lambert W-function. Equation (2) was fitted to the IV response (Figure 2) of the CNT device shown in Figure 1 using the Levenberg–Marquardt algorithm; the obtained fitting parameters are given in Table I. With zero gate bias, a good fit to the data using Eq. (2) can be obtained, except in the high negative bias region which showed evidence of breakdown at around $-2\ \text{V}$. Fitting the IV data obtained at zero gate bias

results in values for η and I_0 of 1.38 and $6 \times 10^{-16}\ \text{A}$, respectively, indicating that both diffusion and recombination occurs. This compares to values obtained for η and I_0 of 1.3 and $8 \times 10^{-10}\ \text{A}$, respectively, for a Sc and Pd asymmetrically contacted CNT diode with a CNT diameter of 3.5 nm.¹³ When our diode is inverted, by applying bias to the gates, η increases to ~ 2 indicating that recombination current dominates. For comparison, graphical analysis of the zero gate bias IV data gives I_0 , R_s , and η parameters of 5×10^{-16} , 1.47×10^7 , and 1.51, respectively. The quality of fit using Eq. (2) in the reverse bias region is reduced when a gate bias is applied. We attribute this to lowering of Schottky barrier heights and/or increased gate leakage current. IV and transfer characteristics were largely unaffected when measured in vacuum or after annealing in a vacuum for 24 h at 300°C indicating that the CNTs are well encapsulated by the Al_2O_3 layer from the atmosphere.

In CNT FETs, it has been shown that current modulation using the gate potential occurs primarily by variation of contact resistance, rather than channel conductance, and the primary effect of oxygen adsorption is to change the work function of the contact metal.²³ Similar device structures to ours have been fabricated by Lee *et al.*⁷ and Bosnick *et al.*,²⁴ however, these devices had symmetric contacts and back-gates. Back-gate geometries should deliver a greater electric field to the metal-CNT contact compared to analogous top-gate geometries.²³ However, with a back gate, CVD must occur following the patterning of the split gates and deposition of the gate insulator oxide. We also fabricated back-gate geometries and found that the gate metal/oxide interface could deteriorate during the CVD process with certain oxide/metal combinations. Additionally, the back-gate geometry leaves the CNTs exposed to the atmosphere. Capacitance-voltage (C-V) measurements of a Pd and Ti asymmetrically contacted CNT diode indicate that the metal-CNT contact is unpinning.²⁵ The inset of Figure 2 shows the device transfer characteristics which indicate that when the split gates have the same potential the device is n-type. This is somewhat unexpected in a device with a high work function Pd contact.

FIG. 2. IV characteristics of the CNT diode at various split gate biases, fitted with an analytical solution to the diode equation. The inset shows the transfer characteristics of the CNT diode with gate 1 = gate 2, and gate 1 only biased with $V_{ds} = -1\ \text{V}$. Band diagrams representing sections of the IV curves marked b–f are shown in Figures 3(b)–3(f), respectively.

TABLE I. Fitting parameters for the IV response of the diode at various split gate biases.

Gate 1 (V)	Gate 2 (V)	η	R_s (Ω)	I_0 (A)
0	0	1.38	1.1×10^7	6×10^{-16}
-5	5	2.01	1.5×10^7	2×10^{-14}
-5	0	1.97	1.4×10^7	2×10^{-13}

However, n-type characteristics have previously been observed from Pd-contacted symmetric devices.²⁶ This was attributed to the small diameter of the nanotube used which increases the work function of the CNT, due to hybridisation, to above that of Pd. Also, the encapsulation of CNTs with Al₂O₃ is also known to effect a p to n-type transition²⁷ due to a change in metal-CNT contact barriers caused by the desorption of oxygen.²⁸ With modulation of gate 1, only (above the Ti contact) the transfer characteristics remain relatively unchanged. This is also unexpected because it implies that electrons can be injected from the Pd contact without any gate bias. This then requires that the Schottky barrier for electrons (Φ_{be}) is smaller at the Pd contact than at the Ti contact. Au has a similar work function to Pd and it has also been observed that n-type conduction can occur in Au-contacted CNT FETs after annealing at 200 °C for 90 h in a vacuum. This was attributed to surface dipoles which it was proposed locally reduce the Au work function.²⁹ The ALD process we used to deposit the gate insulator has similarities to the annealing used in²⁹ as the device was held at 300 °C in a vacuum for 1 h before deposition of Al₂O₃. We therefore propose that the best explanation for the lower Φ_{be} at the Pd contact than at the Ti contact is that surface dipoles form at the Pd contact during annealing, which locally reduce the Pd work function, and that these dipoles do not occur at the Ti contact.

The Fermi level of the CNT in our device should be close to the conduction band, as indicated by the transfer characteristics. The ability to invert the diode by applying a negative bias to the gate above the Ti contact shows that both holes and electrons can be injected from this contact, which supports placing of the work function of Ti close to the middle of the CNT bandgap. On the basis of this discussion, we propose the band diagram model in Figures 3(a)–3(f) to explain the IV characteristics of the CNT diode, the relevant band diagram is marked on the IV curves in Figure 2. At thermal equilibrium, Figure 3(a), the Fermi level (E_F) is shown close to the conduction band, Φ_{be} is shown as larger at the Ti contact than at the Pd contact. In forward bias, Figure 3(b), the Schottky barrier at the Ti contact is thinned allowing electrons to tunnel through. In reverse bias, Figure 3(c), electrons can easily cross the Schottky barrier at the Pd contact but are trapped by the larger barrier at the Ti contact. When positive bias is applied to gate 1 only (see inset of Figure 2) the Schottky barrier at the Ti contact is thinned allowing electrons to tunnel through from the CNT. With a positive drain bias and a negative bias on gate 1 (above the Ti contact) electron injection is blocked by an increased barrier, though a small number of holes may still be injected from the Pd contact, which explains the relatively higher leakage current (see Figure 3(d)). When gate 2 is then negative biased, Figure 3(e), minority carriers from the Pd electrode are blocked, reducing the leakage current. With a negative drain bias and negative and positive bias to gates 1 and 2, respectively, the barrier to hole injection from the Ti contact is reduced (Figure 3(f)).

In conclusion, a single CNT diode, with Ti and Pd contacts and split gates has been fabricated and characterised. Without any applied gate bias the device displays strong rectification with a leakage current of 6×10^{-16} A and an

FIG. 3. Proposed band diagrams for the Ti (source), Pd (drain) CNT diode (a) at thermal equilibrium (the position of E_F is shown), (b) positive drain bias with no split gate bias, (c) negative drain bias with no split gate bias, (d) positive drain bias with negative gate 1 bias only, (e) positive drain bias with negative gate 1 and positive gate 2 bias, and (f) negative drain bias with negative gate 1 and positive gate 2 bias. Solid and dashed lines represent majority and minority carriers, respectively. Blue and red circles represent electrons and holes, respectively.

ideality factor of 1.38. When the gate above the Ti contact is negatively biased, the diode becomes inverted. When a positive bias is then applied to the gate above the Pd contact minority carrier injection is suppressed reducing gate leakage current. In this situation the leakage current and ideality factor were found to be 2×10^{-14} A and 2.01, respectively. The diode parameters were extracted using an analytical solution to the diode equation including a series resistance using the Lambert W-function which offers advantages over conventional graphical methods. Transfer and IV characteristics indicate that the Schottky barrier height for electrons is lower Pd contact than for the Ti contact. This may be due to the preferential formation of dipoles at the Pd contact during the ALD processing.

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