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Solution Processable High Performance Multiwall Carbon Nanotube-Si Heterojunctions

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Abstract

Carbon nanotube (CNT)-silicon (Si) heterojunctions show exceptional electrical behaviour and hence are promising for electronic and optoelectronic applications. In particular, singlewall CNTs (SWCNTs)-Si heterojunctions have been widely studied for these applications. Since multiwall CNTs (MWCNTs) have higher electrical conductivity than SWCNTs, engineering the properties of MWCNTs so as to tailor their electrical properties suitable for heterojunctions can boost the performance of CNT-based electronic and optoelectronic devices. Here we report the development of MWCNT-Si heterostructures, following surface functionalization and silanization to tailor their structure and properties, at room temperature via solution processing. The developed Al/*n*-Si/MWCNT/Al heterojunction devices shows a low turn-on voltage (~1-3 V) and high current (~0.8 mA at 10 V) exceeding the previous high temperature processed CNT-based heterojunctions as well as room temperature grown additional amorphous carbon–Si heterojunctions. We discuss the carrier transport mechanism within a carrier-selective contact, multi-junction, multi-resistance framework, with device current-voltage behavior dictated by transport across the heterojunction and quantum tunneling. This work opens new direction to design improved devices for future development of large area solution processable CNT based electronics.

Introduction

Heterostructure devices composed of electronic materials offer extraordinary characteristics allowing their application in diodes, transistors, solar cells, and photodetectors.¹⁻⁹ van der Waals heterostructures⁵⁻⁷ and oxide heterostructures^{8,9} are two families of low-dimension heterojunction-based devices expected to advance electronics and optoelectronics to the next generation. Recent examples include graphene-perovskite-graphene and graphene-WSe₂-perovskite-graphene heterojunctions², carbon nanotube-MoS₂ *p-n* junction diodes³ and graphene-silicon Schottky diodes⁴, graphene-hBN (hexagonal boron nitride), WSe₂-MoS₂, and MoS₂-pentacene heterojunctions⁵⁻⁷, and a variety of oxide heterostructures/superlattices structures^{8,9} which have variously been employed in developing high performance electronic, optoelectronic, and spintronic devices. Carbon nanotubes (CNTs) are a particularly important class of materials which have already demonstrated a broad spectrum of applications.^{1,3,10-20} Their one-dimensional structure and their strong in-plane bonding and delocalized π electrons, coupled with an ability to functionalize their surface, enables a wide range of attractive electronic and mechanical properties along with chemical stability. Owing to their high electron mobility and electrical conductivity, along with their compatibility with high-*k* dielectrics, CNTs are ideal for nanoscale electronic devices such as field effect transistors (FETs);¹⁰⁻¹² researchers from IBM have developed the first CNT-based computer.^{15,16} CNTs can also display excellent electrical properties in a heterojunction configuration, for example, CNT-MoS₂ (ref. 3), and CNT-Si heterojunctions¹⁷⁻²⁰ have been developed for multiple applications. In particular, CNT-Si heterojunctions have attracted considerable interest for solar cells applications.²¹⁻²⁸ Yu *et al.*²¹ developed singlewall carbon nanotubes (SWCNT)-Si heterojunction for solar cells and realized an efficiency above 10%. Bat-Erdene *et al.*²² developed SWCNT-Si heterojunction solar cells with an efficiency of ~7.55% which was further increased to ~9.3% by introducing black phosphorous in SWCNT-Si heterojunction. Remarkably, Chen *et al.*²³ have recently observed about 15.2-18.9% efficiency in CNT-Si

heterojunction solar cells. Thus, CNT-Si heterojunction for solar cells is an exciting area of research but more focus is paid on SWCNTs for these heterojunction devices so far. Since the electrical conductivity and mobility of MWCNTs is higher than semiconducting SWCNTs, the modification of properties of MWCNTs so as to make them suitable for heterojunction devices would enable the development of high-performance optoelectronic devices.

High temperature processing is another critical concern for CNTs-based systems.^{10-13,29,30} Chemical vapor deposition (CVD) and plasma enhanced chemical vapor deposition (PECVD) are the two most widely used methods that require the use of catalyst- and high temperature processing for direct growth of CNTs onto the substrates.^{30,31} In general, the temperature requirement for high quality CVD-grown CNTs typically exceeds 800°C.^{19,31} Similarly, PECVD uses high temperatures above 500°C in most cases³⁰, although the growth of CNTs has been demonstrated between 120-200°C with the aim of minimizing the thermal budget.^{30,32} Thus, the high temperature growth of CNTs directly on technologically relevant substrates restricts their wide-spread application. The growth of CNTs using standard processes followed by solid-phase transfer onto the substrate is another route to transfer onto a larger area though complete substrate coverage is difficult to attain.³³ Solution-processing and wet chemistry represent a scalable route to deposit CNT coatings³⁴⁻³⁶ at low temperature, with fabrication of solution-processed CNT-based high-speed logic integrated circuits³³ and thin film transistors³⁵ having been reported. Electrophoretic deposition, which uses both solution chemistry and an electric potential, can be superior to other solution-based methods (such as spin coating, dip coating, and solution casting) in terms of CNT coating quality and adhesion of the coating to the underlying substrate.³⁷ While solution processed CNT-based coatings on substrates have been applied for various applications such as biosensors¹⁴ and field emission,²⁹ the production of high quality MWCNT-based heterojunction devices with semiconducting type electrical transport in heterojunction is not well explored. Moreover, the effects of

functionalization and silanization on the electrical transport of MWCNT-based heterojunctions are not well understood to date.

In this work, we report the fabrication and characterization of MWCNT-based heterojunction devices (Al/*n*-Si/MWCNT/Al structure) by solution-based electrophoretic deposition. The devices form three distinct electrical junctions, namely, metal (Al)–*n*-Si, *n*-Si–MWCNT, and MWCNT–Al junctions (the *n*-Si–MWCNT heterojunction will be referred to as the CNT–*n*-Si heterojunction hereafter). We observe both ohmic and non-ohmic I-V electrical behavior with a low turn-on voltage and high current when measured in a sandwich electrode configuration. The characterization and analysis show that CNT–*n*-Si and CNT–Al junctions contribute to non-ohmic I-V behaviour which is supported by extensive characterization of our CNT coatings. The electrical performance of these CNT-based heterojunction devices is compared with other carbon-based heterojunction devices, specifically amorphous carbon (a-C)/Si heterojunction devices where the a-C films are grown at room temperature using a PECVD process.^{38,39} The electrical resistance in our CNT-based heterojunction devices is considerably lower than a-C/Si heterojunction devices. The electrical behavior is analyzed to understand the factors that control electrical transport in these Al/*n*-Si/CNT/Al heterojunction/multi-junction devices. These results open a new direction of research to utilize low-cost and solution processable MWCNTs as an alternative to SWCNT heterojunction devices.

Experimental: Fabrication of CNT-Si Heterostructures

MWCNTs were prepared using catalytic CVD with iron as the catalyst obtained by the decomposition of ferrocene and toluene as the hydrocarbon source.^{14,40} The temperature for the growth of MWCNTs was kept at ~750°C. The CNTs were then purified and functionalized using a boiling acid treatment¹⁴; this functionalization modifies electrical and optical properties of CNTs.⁴¹⁻⁴⁵ To construct a platform for heterojunction devices by applying the CNTs at room

temperature, the CNT coatings were made on well-cleaned *n*-type crystalline silicon (resistivity 0.001–0.005 Ωcm and thickness 500–550 μm) using DC-controlled electrophoretic deposition, as described in detail elsewhere.¹⁴ The required colloidal suspension (10 ml) to enable thin coatings was prepared by diluting a 100 μl stock solution of CNT (1 mg/ml in acetonitrile) in 9.9 ml of acetonitrile. Since the application of organosilane, such as 3-aminopropyltrimethoxysilane (APTES), has been found to enhance the adhesion, dispersion and properties of CNTs^{46,47}, here a 20 μl of APTES was also added to the colloidal mixture. Prior to CNT deposition, the *n*-type crystalline silicon (c-Si) substrates were cleaned using standard RCA cleaning followed by a hydrofluoric acid dip, rinsed in de-ionized water, and finally dried using nitrogen gas. To produce the CNT coatings, a static potential difference was applied between the two electrodes, **Figure 1**. As our preliminary research suggested the formation of CNT coatings with good substrate coverage at DC voltages around 180–200 V, we selected this voltage range to produce final CNT coatings. The total time for CNT deposition for each CNT film was kept at 30 s. For the first (CNT-1) and second (CNT-2) CNT–Si heterostructure samples, DC voltages of 180 V and 200 V, respectively, were used. The third CNT–Si heterostructure sample (CNT-3) comprised a bilayer CNT coating in which the first layer was deposited at 180 V (for 15 s) and the second layer was deposited at 200 V (for 15 s). Thus, the total time for CNT deposition in all three samples was kept the same; sample details are summarized in Table 1.

Table 1: Details and nomenclature of various CNT/Si heterostructure samples used in the present work.

Sample label	DC Voltage for CNT Deposition (V)	CNT Film Thickness (nm)
CNT-1	180	120 $\pm$ 10
CNT-2	200	130 $\pm$ 10
CNT-3	180 and 200	128 $\pm$ 10

Figure 1: Schematic illustration for the production of CNT coatings. (a) We used CNTs in powder form and subsequently functionalized them with carboxyl groups to form a CNT dispersion in acetonitrile solution. (b) Electrophoretic deposition was employed to produce the CNT coatings. APTES was added to the CNT and acetonitrile solution to enhance the adhesion of the CNT coatings to the substrate. Once the selected potential difference was applied between the two electrodes, the deposition of CNT on *n*-Si was activated, and finally the CNT coatings were realized on *n*-Si. (c) As an example, we also illustrate possible interactions between the CNT, functional groups, and APTES.

Results and Discussion

After sample fabrication, the CNT films were characterized for thickness, structure, and chemical bonding. The thickness of each CNT film was measured using a Talystep profilometer (Taylor-Hobson, UK) attached with a diamond stylus; all CNT films were in a narrow average thickness range of 120 - 130 nm. High resolution field emission scanning electron microscopy (FE-SEM) was used to investigate the morphology of the CNT thin films; the captured images are presented in **Figure 2**. Closer inspection of the images shows that the diameters of CNT bundles in samples CNT-2 and CNT-3 are smaller than in sample CNT-1. All the samples revealed the presence of entangled CNTs throughout the surface. Furthermore, the nanotubes are observed to be more bundled with a lower dispersion in sample CNT-1 as compared to samples CNT-2 and CNT-3. Sample CNT-2 yielded the highest dispersion of CNTs among the three. Additionally, since APTES was added to the colloidal mixture of MWCNTs for film deposition, the traces of silane coatings are also found in SEM images, verified by infrared spectroscopic analysis discussed later.

Raman spectroscopy is a widely employed method to assess the quality and structural properties of CNTs and other carbon materials.^{31,40} These measurements were performed with a Renishaw inVia Reflex micro-Raman spectrophotometer (514.5 nm excitation). We first recorded the Raman spectra of starting MWCNTs materials on three different locations, **Figure 3a-3c**. The Raman spectra of starting MWCNTs material reveal well defined D and G peaks as well as D' peak. The complete Raman spectra of starting MWCNTs material in the range of 1200-3000 cm^{-1} , which displays 2D peak location as well, is presented in **Supplementary Information S1 (Figure S1)**. The fitting of Raman spectra (not shown here) was performed to find the exact D and G peak locations and the intensity ratio of D to G peaks (I_D/I_G). The G peak position for starting MWCNTs material is found to be at 1579 cm^{-1} for location 1, 1580.5 cm^{-1} for location 2, and 1579 cm^{-1} for location 3. Likewise I_D/I_G ratio for starting MWCNTs material is measured to be 0.32 at location 1, 0.31 at location 2, and 0.42 at location 3. The

results of G peak position for all the three locations correspond to the characteristic peak of MWCNTs, and observation of D and D' peaks indicate that the MWCNTs have some disorder in their structure.

Next, we measured the Raman spectra of CNT coatings, namely, samples CNT-2 and CNT-3. The Raman spectra of samples CNT-2 and CNT-3 reveal the D and G peaks at ~ 1350 cm^{-1} and ~ 1580 cm^{-1} , respectively, and the D' and 2D peaks at ~ 1620 cm^{-1} and ~ 2705 cm^{-1} , respectively (see **Supplementary Information 1, Figure S2**). The presence of well-defined G and 2D peaks along with the FE-SEM images (**Figure 2**) confirm the coatings of CNTs, and the observation of D and D' peaks indicate that the coated CNTs also have disorder in their structure; the examination of the I_D/I_G ratio was used to characterize the disorder present. To quantify the disorder in CNT coatings, we first fitted the D and G peaks using a Lorentzian function to extract the D and G peak positions (**Figure 3d and 3e**), and calculated the I_D/I_G intensity ratio, and the area ratios of the D peak to the G peak (A_D/A_G). The D and G peaks in sample CNT-2 were observed at 1352 cm^{-1} and 1582 cm^{-1} , respectively, which is similar to those found in sample CNT-3 (1351 cm^{-1} and 1581 cm^{-1} , respectively). The I_D/I_G (A_D/A_G) ratios in sample CNT-2 and CNT-3 were measured to be 0.59 (0.67) and 0.62 (0.73), respectively. These results suggest that there is negligible difference in the structure and disorder of the CNTs in these samples, though CNT-2 has a slightly less disordered structure than CNT-3. However, with respect to starting MWCNTs material that shows I_D/I_G ratio of 0.31-0.42 the observed slightly higher I_D/I_G ratio ~ 0.59 -0.62 in CNT coatings suggest that both the material preparation for the coatings and the coating process increase the disorder in CNTs. It means surface functionalization of MWCNTs and electrophoretic deposition process increase the disorder in CNTs. Nonetheless, Bayer *et al.*⁴⁸ found an I_D/I_G ratio of about 0.9 for a CNT film directly grown on Si at a higher temperature of ≥ 650 $^{\circ}\text{C}$ using a catalyzed CVD process and concluded it to be a reasonable quality CNT film. Thus, the observation of a relatively lower I_D/I_G ratio in

our two-step processed and functionalized CNT coatings on Si demonstrates production of good quality CNT films at room temperature.

Figure 2: Morphological characterization: representative scanning electron microscopy images of all samples CNT-1, CNT-2, and CNT-3.

Figure 3: Raman and XPS analysis of samples. Raman spectra of starting MWCNTs material taken on three different locations (a) location 1, (b) location 2, and (c) location 3. Raman spectra of CNT coatings after fitting of the spectra for (d) CNT-2 and (e) CNT-3. The fitting was performed using two Lorentzian components to get the exact D and G peak positions, and I_D/I_G and A_D/A_G ratios of samples. (f) XPS measurements were performed on samples CNT-1 to CNT-3. (f) Deconvolution of high resolution XPS C 1s spectra for different CNT coatings. The deconvolution was performed using four Gaussian components with background subtracted using the Shirley method.

The surface chemistry of the CNT coatings was examined using x-ray photoelectron spectroscopy (XPS) using Al K α (1486.6 eV) photons in a Perkin Elmer 1257 instrument operating under ultrahigh vacuum conditions. The deconvolution of the C1s spectra was performed using the Shirley background subtraction method⁴³ with various Gaussian

components to get a good fit to the data, **Figure 3f**. The deconvolution of each spectrum shows one major peak, C₁, located at ~284.5 eV along with three relatively weaker peaks C₂, C₃ and C₄ centered at ~285.4 eV, ~286.3 and 288.9±0.1 eV, respectively, suggesting the presence of different carbon bonding configurations. Generally, the sp² bonded carbon peak in the C1s spectra of CNT and other carbon materials is observed between 284.0 - 284.6 eV.⁴⁹⁻⁵² In particular, the peak corresponding to sp² bonding in CNTs was reported to be situated at 284.3-284.6 eV by Hofmann *et al.*⁴³ and at 284.1-284.2 by the Moraitis *et al.*⁵⁰ Therefore, we attribute the C₁ peak, the major peak in the C 1s spectra, as the characteristic XPS peak of CNTs. The relatively weaker C₃ and C₄ peaks are assigned to C-O and C=O/O-C=O, respectively⁴⁸, and suggest the presence of functional moieties arising from successful functionalization of CNTs. Since peaks C₁, C₃, and C₄ typify the carbon bonding expected from these CNT coatings, the observation of the C₂ peak indicates that some other type of carbon-based bonding is also present in the coatings. For a sp² bonded carbon system, whether CNT or graphene, Hofmann *et al.*⁴³ and Kidambi *et al.*⁵¹ observed a weak peak located close to 285.4 eV, similar to the position of the C₂ peak in our case, and they assigned it to disordered carbon with partially increased sp³ hybridization. Thus, we also assign the C₂ peak as originating from bonding associated with disordered carbon with partially increased sp³ bonded carbon arising from the functionalization and acid treatment of CNTs during the preparation of CNT solutions. We also calculated the area ratios of the C₁/C₂ peaks which were found to be 5.5, 6.4 and 5.9 in CNT-1, CNT-2 and CNT-3, respectively. Thus, sample CNT-2 yielded the highest C₁/C₂ peak area ratio which signifies the presence of relatively better quality CNTs with respect to samples CNT-1 and CNT-3. Additionally, the FTIR spectrum of the selected sample CNT-2 is also recorded which reveals the characteristic peak of CNTs and various peaks pertaining to functional moieties such as -COOH and silane (see **Supplementary Information 2** for details). Overall, SEM, Raman, XPS, and FTIR characterization confirm the formation of good quality CNT

films, and the traces of silane coatings on MWCNTs are also observed which is expected to influence the electrical transport of our MWCNTs-based heterojunctions.

Next, aluminium (Al) was thermally evaporated onto the CNT-Si heterostructures as well as on the contact area of the silicon substrate to create device contacts for electrical characterization (**Figure 4a**). The thickness of Al contacts was measured to be ~90 nm. The current-voltage (I-V) characteristics were recorded in an ambient atmosphere using a Keithley 4200 sourcemeter. The I-V curves of our Al/*n*-Si/CNT/Al devices (**Figure 4(b)-(d)**) initially display ohmic behaviour that then deviates from linear at higher voltages. Non-ohmic I-V behaviour has been previously reported in high temperature grown singlewall CNT-metal heterojunctions⁵³, and a weak non-linear I-V transport in high temperature grown multiwall CNT-Si heterojunctions.⁵⁴ At large bias, the current deviates slightly between the devices; for example, the magnitude of current at 10 V (labelled I_{10}) for devices CNT-1, CNT-2, and CNT-3 is 45 μ A, 800 μ A, and 100 μ A, respectively.

From the transition of ohmic to non-ohmic I-V curves, we estimate the turn-on voltage (V_{on}), and apply various models to describe the shapes of the I-V curves. V_{on} is defined as the voltage at which the I-V curve deviates from linearity in the initial (low) bias voltage regime. In **Figure 5a**, log-log I-V plots are linearly fitted (slope = 1) to show more clearly the deviation from linear behavior. The log-log I-V curves (**Figure 5a**) indicate linear behaviour at low voltages (up to about 1-3 V) and the re-emergence of a linear behavior at high voltages (from about 5-6 V to 10 V). Between the two regimes, a non-linear transition regime can be seen. Additional discussion highlighting low- and moderate-bias behavior is included in the **Supplementary Information 3**. Using log I vs. log V plots, we estimated V_{on} to be ~2.5 V for CNT-1, ~1.1 V for CNT-2, and ~2.4 V for CNT-3, respectively. Interestingly, the value of V_{on} in our solution-based room temperature grown CNT-based devices (1.1-2.5 V) is observed to be comparable to higher temperature grown CNT-based devices.^{55,56}

Figure 4: (a) A schematic of device configuration used for I-V measurements of Al/*n*-Si/CNT/Al heterojunctions. The active device area is 0.785 mm^2 , defined by the top Al contact on CNT. I-V curves for (b) CNT-1, (c) CNT-2, and (d) CNT-3 devices recorded at room temperature. (e) I-V scans of Al-*n*-Si contacts that show consistent linearity, therefore verifying the ohmic behavior at the Al-*n*-Si junction.

Nonlinearity can also be quantified from the I-V curves as the ratio of the differential conductivity to the secant conductivity (**Figure 5b**), $N = \frac{dI/dV}{I/V}$, which is widely used in investigating rectenna devices.^{57,58} In this method, V_{on} is the voltage at which the nonlinearity

exceeds and remains above a value of 2 (a value selected to highlight a transition into nonlinear behavior). Among the three devices, CNT-2 shows the significant nonlinear behaviour, which increases gradually and smoothly up to a value of $N = 3$ at high bias (**Figure 5b**). At low bias near 0.3 V, CNT-1 and CNT-2 begin to show some nonlinearity with $N > 1$ in **Figure 5b**, and an onset of transition from linear to weak non-linear I-V behavior in **Supplementary Figure S4**. While studying the electrical transport properties of CNTs by two-probe measurements, Barnett *et al.*⁵⁹ observed a small nonlinearity, an onset of transition from linear to weak non-linear I-V behaviour (in the 0-1 V range) due to the presence of contamination at the interface of the probe and the CNTs. Similarly, Kawano *et al.*⁶⁰ noticed a slight nonlinearity in an otherwise ohmic I-V curves (0-1 V range) of a single CNT. Recently, Piquemal-Banci *et al.*⁶¹ also observed a weak non-linearity between 0-0.2 V in a Co/h-BN/Fe system and they assigned it to tunneling behaviour. In our case, some nonlinearity up to 0.3 V could be ascribed to these factors, especially the tunneling of the carriers near metal-semiconductor interface; however, we observed significant nonlinearity in the I-V curves beyond 3 V in all devices after diode turn-on occurred. From **Figure 5b**, we estimate V_{on} to be 3.0, 1.6, and 2.8 V for devices CNT-1, CNT-2, and CNT-3, respectively. Thus, the values of V_{on} found through this method are consistently ~ 0.5 V higher than when using a log-log I-V method. Therefore, though this nonlinearity method gives a slightly higher bound for V_{on} estimation, the trend of V_{on} is found to be same with respect to log-log I-V method.

Figure 5: Carrier transport analysis. (a) I-V behavior of different devices plotted on log-log scale. Fitted lines are shown to illustrate the ohmic transport regimes. (b) Nonlinearity (ratio of differential conductivity to secant conductivity) as a function of voltage. (c) Semi log I-V plot to illustrate diode-like behavior, (d) $\log I$ vs $V^{1/2}$ dependence to illustrate Schottky-like behaviour and (e) $\log I$ vs $V^{-1/4}$ dependence to illustrate hopping/tunneling-like behavior. (f) Electrical resistance of CNT-Si heterojunctions at input voltages from 1-10 V. For comparison, the electrical resistance of room-temperature grown amorphous carbon/Si heterojunction devices is also included (ref. 30). The dashed line indicates the average electrical resistance (at 10 V) of all three CNT-Si heterojunctions.

We now discuss the potential transport mechanisms of these CNT-*n*-Si based heterojunction devices. The electrical transport in the proposed devices can be explained by the formation of three junctions connected in series (**Figure 4a**): (i) Al-*n*-Si, (ii) CNT-*n*-Si, and (iii) CNT-Al junctions. The Al-*n*-Si contact would act as electron selective contact while CNT-Al would act as hole selective contact. We discuss all these junctions one by one. The work functions of Al (ϕ_{Al}), *n*-Si (ϕ_{Si}), and CNT (ϕ_{CNT}) are 4.0-4.2 eV, 4.3-4.7 eV, and 4.3-5.0 eV, respectively⁶²⁻⁶⁶, indicating $\phi_{\text{Al}} < \phi_{\text{Si}}$ and $\phi_{\text{Al}} < \phi_{\text{CNT}}$. We first discuss the Al-*n*-Si contact based on the known Al and *n*-Si work functions, knowing that the electron affinity (χ) of c-Si is comparable to the Al work function, the resulting barrier height, based on the Schottky model⁶⁶ is negligible ($\phi_{\text{b}} = \phi_{\text{Al}} - \chi_{\text{Si}}$, ϕ_{Al} is 4.0-4.2 eV and χ_{Si} is 4.05 eV). Hence, we predict Al-*n*-Si ohmic contact between Al and *n*-Si. Indeed, evaporated Al is widely used to make ohmic contacts to both *n*-Si and *p*-Si provided that the conductivity of c-Si is suitably high and any potential barrier between the Al and c-Si is thin enough to be effectively electron transparent.⁶⁷ For instance, Northrop and Puddy⁶⁷ realized good ohmic contact between Al and *n*-Si, with *n*-Si resistivity of 0.5 Ω -cm. Ohmic transport in a similar system with *n*-Si resistivity of 0.5-2.0 Ω -cm was also reported by various other researchers.^{68,69} In our case, the resistivity of *n*-Si (0.001-0.005 Ω -cm) is much lower than reported in Refs. (64, 65), suggesting the formation of an ohmic contact between Al-*n*-Si. We confirmed this by measuring the electrical behavior of isolated Al-*n*-Si contacts and verified our contacts to be ohmic (**Figure 4e**).

Next, since Al-*n*-Si contact reveals linear I-V (ohmic) transport, the non-ohmic transport in I-V curves of Al-*n*-Si-CNT-Al devices must originate from either the CNT-*n*-Si contact or CNT-Al contact or both contacts. Our MWCNTs seem to have a non-linear electrical behaviour which could originate from 1) the presence of defects, sp³-like defects, and disordered carbon, and 2) functionalization (boiling acid treatment) and silanization of MWCNTs (addition of APTES), all of which alter the properties of MWCNTs. It is well

established that the functionalization and interaction with oxygen-related moieties (such as -COOH and -OH groups), as well as the presence of disordered carbon and sp^3 -like defects, produce and alter the band gap and induce weak p -type semiconducting behavior in CNTs.^{42-45,54,62} For MWCNTs in particular, the presence of even minor structural defects is known to drastically change their electrical properties.^{70,71} For example, Ref. 70 shows a non-linear I-V transport in MWCNTs due to presence of defects. Cole *et al.*⁴⁵ found a low band gap in MWCNT with weak p -type character. Lee *et al.*⁵⁴ also observed mild p -type semiconducting behaviour in MWCNT, and the behaviour across a MWCNT-MWCNT heterojunction revealed a non-linear I-V transport. Moreover, in our case besides aforementioned surface and structural changes, the silanization of MWCNTs, i.e., coating of silane is expected to tailor the electrical properties of MWCNTs also contribute to a non-linear electrical transport in MWCNTs. While CNT-Al contact is expected to act-like a hole selective contact, however, due to small work function difference between CNT and Al, $\phi_{Al} < \phi_{CNT}$ there will be Schottky energy barrier. Thus, the non-linear I-V response in Al/ n -Si/CNT/Al system likely originates from the CNT- n -Si heterojunction contact with some contribution from CNT-Al contact.

Next, we examine the I-V curves in view of various transport models. Since heterojunction diode current depends exponentially on bias (equation 1), a semi-logarithmic graph ($\log I$ vs V) is plotted in **Figure 5c**. The devices CNT-1, and especially CNT-3, demonstrate typical heterojunction contact behavior. After ~ 4 V, CNT-1 appears to deviate from this trend. However, CNT-2 does not appear to fit the ideal diode model after the initial 1-2 V, suggesting that other transport mechanisms dominate. Thus, we explore additional transport models in semiconducting networks *via* the Schottky transport model. The field-dependent conductivity σ (a function of current) can be expressed as³⁹

$$\sigma = \exp\left(-\frac{E_a - f(E)}{kT}\right) = \sigma_0 \exp\left(\frac{f(E)}{kT}\right) \quad (1)$$

where E is the electric field which is a function of V , E_a is the activation energy, k is Boltzmann's constant and T is the temperature (room temperature). Schottky emission occurs when electrons hop over reduced energy barrier directly into the conduction band and is both field- and temperature-dependent.⁷² It can be seen through a linear dependence when plotting $\log(I)$ vs. $V^{1/2}$ (**Figure 5d**). Tunneling and hopping transport are also possible in semiconductors with defects. Tunneling occurs from states near the Fermi level or from a weak barrier, whereas hopping from one state to another is possible when the states are close together. Typical hopping/tunneling follows a $I \sim \exp(V^{-1/4})$ dependency (**Figure 5e**).⁷² It has already been established that ohmic behaviour is primarily observed for all devices at low bias. Around 2 V, the device CNT-1 begins exhibiting good heterojunction diode-like behavior, though around 4 V the high-bias performance seems to transit to Schottky emission. In device CNT-3, there is strong dependence on Schottky emission over a large bias range (2-9 V) in addition to heterojunction diode-like behavior. The actual $\log I$ power-law dependence is $V^{0.7}$, signifying that both mechanisms are prevalent over the extended voltage range. Finally, in CNT-2 we find that the ideal diode condition does not fit well for a large range; a one-diode fit is obtained in initial ~1-2 V range and the Schottky emission is observed thereafter. At high bias, all devices begin to exhibit some manner of $V^{-1/4}$ dependence. This indicates electrical transport influenced by hopping or tunneling mechanisms, mainly from the states available near the Fermi level in the Al/*n*-Si/CNT/Al system.

Finally, the discussion returns to band diagram consideration of the Al/*n*-Si/CNT/Al heterojunctions. **Figure 6** shows the band diagrams of the individual components before contact (**Figure 6a**) and the band diagram of the system after contact (**Figure 6b**).

Figure 6: Carrier transport model for Al/Si/CNT/Al system. Energy band diagrams of individual materials (a) before contact and (b) after contact. Solid circles represent electrons while open circles represent holes. The black dashes near Al-Si and Al-CNT interfaces represent the defects.

Upon contact formation and Fermi level equalization, band bending occurs, resulting in a built-in potential (V_{bi}) at the Al-CNT junction as expressed by

$$eV_{bi1} = e\phi_{CNT} - e\phi_{Al} \quad (2)$$

The difference in band gap (E_g) between the CNT and the n -Si leads to the origin of conduction band (ΔE_C) and valence band (ΔE_V) offsets at the CNT-Si junction, and the sum of the band offsets can be expressed by the difference of the band gap (ΔE_g) of two materials:

$$\Delta E_g = E_{g(Si)} - E_{g(CNT)} = \Delta E_C + \Delta E_V \quad (3)$$

Because of the band bending, a second built-in potential, V_{bi2} , is formed at the CNT-Si junction, which is the sum of the band bending on n -Si and p -side of the junction,

$$eV_{bi2} = E_{g(CNT)} - (E_F - E_V)_p - (E_C - E_F)_n + \Delta E_C \quad (4)$$

Once the junction has been established, carrier transport is achieved by applying an external potential difference.

Next, we can also estimate the secant resistance of the devices fabricated here and compare the results with other room temperature processed carbon-silicon heterojunction systems as well as high temperature grown CNT-based heterojunction devices. In this regard, amorphous carbon (a-C) is a classic carbon material we use for comparison as it is usually deposited at room temperature and possesses different amount of sp^3/sp^2 bonding. We fabricated amorphous carbon-Si (a-C-Si) heterostructures at room temperature with the a-C films produced by PECVD. Two different types of a-C were deposited for comparison: hydrogenated amorphous carbon (a-C:H), and nitrogen incorporated hydrogenated amorphous carbon (a-C:H:N). Al contacts were deposited to form heterojunction devices similar to the CNT-Si heterostructures, with similar dimensions for direct comparison of electrical characteristics. The a-C:H-*n*-Si and a-C:H:N-*p*-Si devices are labelled as a-C and a-CN, respectively. The secant resistance, $R_{sec} = \frac{V}{I}$, is reported in **Figure 5f** for specific biases. Our solution grown CNT-based heterojunction devices exhibit much lower electrical resistance than the plasma-processed a-C-Si and a-CN-Si heterojunction devices by three to five orders of magnitude. Other studies on high temperature grown CNT-based heterojunctions, e.g., Yang *et al.*⁵³ reported secant resistance of $1.3 \times 10^5 \Omega$ for a high temperature (1000 °C) grown CNT-based heterojunction devices, Hu *et al.*¹⁷ found secant resistance between $2.5-17 \times 10^7 \Omega$ in a high temperature (600 °C) grown CNT-silicon nanowire heterojunctions, and Lu *et al.*⁷³ reported around $3 \times 10^6 \Omega$ in a high temperature CVD grown CNT-metal heterostructure. Thus, the resistance of our room temperature grown CNT-based heterojunction devices is comparatively lower than high temperature grown CNT-based heterojunctions. Overall, these results reinforce the development of good quality CNT-based heterojunction devices at room temperature.

We propose an equivalent circuit model to discuss the electrical resistance in these devices. As the devices possess multiple junctions, the resistance will be dependent on the bulk resistance of each material as well as the resistance between each material interface. The overall resistance can be expressed as the sum of all the bulk and interface resistances:

$$R = R_{\text{Al-Si}} + R_{\text{Si}} + R_{\text{Si-CNT}} + R_{\text{CNT}} + R_{\text{CNT-Al}} \quad (5)$$

$$R = R_{\text{Al-Si}} + R_{\text{Si}} + R_{\text{Si-aC}} + R_{\text{aC}} + R_{\text{aC-Al}} \quad (6)$$

where R_{Al} , R_{Si} , R_{CNT} , and R_{aC} are bulk resistances, and $R_{\text{Al-Si}}$, $R_{\text{Si-CNT}}$, $R_{\text{Si-aC}}$, and $R_{\text{aC-Al}}$ are interfacial resistances. In the above relations, we assume the resistance of Al is negligible due to its high conductivity. From equations (5) and (6), it is noted that the final three resistances distinguish Al-Si-CNT-Al heterojunctions from Al-Si-a-C-Al heterojunctions and hence govern the transport in various carbon-based systems examined here. The conductivity of CNTs is much higher than amorphous carbon. In carbon-based materials the electrical transport is predominantly governed by the sp^2 bonding and sp^2 clustering. The carbon material with high sp^2 bonding shows higher electrical conductivity than the inferior electrical transport of sp^3 bonded carbon. A CNT is comprised mainly of a sp^2 -bonded carbon network while amorphous carbon possesses the mixture of both the sp^3 and sp^2 bonding as well as the presence of hydrogen when deposited using the PECVD process, similar to the present case. Thus, the bulk electrical resistance of CNT is much lower than the bulk resistance of amorphous carbon ($R_{\text{CNT}} \ll R_{\text{a-C}}$) which is the predominant reason for lower resistance in CNT-based devices. The lower resistance in a-CN devices compared to a-C devices can be attributed to the incorporation of nitrogen to enhance the sp^2 bonding of amorphous carbon.³⁸ Besides bulk resistance, the interfacial resistances are also expected to have influence on overall resistance of these devices.

The small difference in electrical resistance between the CNT-based devices can be correlated to the quality of the CNTs in different samples. We recall that our CNTs possess a deleterious carbon: disordered carbon with partially increased amount of sp^3 bonded carbon. This was confirmed by the observed D peak in Raman spectroscopy and peak C_2 in XPS analysis (peak C_1 represents the CNT peak in XPS). Since the amount of disorder in carbon and defects is lowest in CNT-2, device CNT-2 exhibited slightly better electrical performance than the other devices. Except for the marginal difference between DC voltages of 180 V and 200 V applied for the respective coatings of CNT-1 and CNT-2, all other parameters are identical. We see 200 V facilitates the growth of higher-quality CNT coatings with fewer defects and less disordered carbon, leading to improved electrical characteristics. Thus, our electrical characterization confirms the formation of excellent CNT-Si heterojunctions with metal contacts and suggests that the quality of CNT films correlate to electrical performance, with lower disordered carbon yielding higher electrical conductivity.

4. Conclusion

We have prepared high quality multiwall CNT-*n*-Si heterostructures at room temperature using a facile and scalable electrophoretic deposition method. The CNT-*n*-Si heterojunctions with metal contacts enable high performance electrical transport and revealed non-linear electrical characteristics which predominantly originate from the CNT-*n*-Si heterojunction with some contribution from the CNT-Al contact that acts as a weak Schottky barrier. The low diode turn-on voltage (~ 1 -3 V) and high current (up to ~ 0.8 mA at 10 V) were realized in CNT-based devices. The electrical resistances of these CNT-based multi-junction were more than three orders of magnitude lower than comparable amorphous carbon-based multi-junction devices. While the interface had some influence on the carrier transport, the bulk resistance of CNT films was estimated to dominate the overall resistance of multi-junction devices. Our findings present a great opportunity for designing cost-effective, high performance CNT-based devices

with improved carrier transport. This establishes an important route for engineering MWCNTs as an active material in novel heterojunction optoelectronic devices and promotes future scientific and technological developments.

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Supporting Information

Solution Processable High Performance Multiwall Carbon Nanotube-Si Heterojunctions

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Supplementary Information 1

Raman spectroscopy: Raman spectroscopy measurements (514.5 nm excitation) were performed with a Renishaw inVia Reflex micro-Raman spectrophotometer. We first recorded the Raman spectra of starting MWCNTs materials in a range of 1200-3000 cm^{-1} on three different locations, Figure S1. The Raman spectra of starting MWCNTs material reveal well defined D and G peaks as well as D' peak. In addition, a 2D peak is also observed. The G peak, which represents E_{2g} zone centre phonons, is attributed to the bond stretching motion of sp^2 carbon atoms. The D peak, which represents the A_{1g} breathing mode of transverse optical (TO) phonons near the K points of the Brillouin zone, and is activated in the presence of disorder in graphitic materials; the D peak originates due to the inter-valley double resonance process. In addition, the Raman spectra (Figure S1) reveal the presence of the D' and 2D peaks. Since the double resonance process can also be possible through an intra-valley route, the D' peak is activated. The 2D peak requires the condition of momentum conservation by two phonons of opposite wave vectors to be satisfied, but does not require the presence of disorder for its activation. The results of G and D peaks position for all three locations correspond to characteristic peak of MWCNTs, and observation of D and D' peaks indicate that the MWCNTs have some disorder in structure.

Next, we measured the Raman spectra of CNT coatings, namely, samples CNT-2 and CNT-3. The Raman spectra of samples CNT-2 and CNT-3 (Figure S2) reveal D and G peaks at $\sim 1350 \text{ cm}^{-1}$ and $\sim 1580 \text{ cm}^{-1}$, respectively. In addition, the Raman spectra of samples CNT-2 and CNT-3 (Figure S2) reveal the presence of the D' and 2D peaks at $\sim 1620 \text{ cm}^{-1}$ and $\sim 2705 \text{ cm}^{-1}$, respectively. The presence of well-defined G and 2D peaks along with the FE-SEM images (main manuscript Figure 2) confirm the coatings of CNTs, and the observation of D and D' peaks indicate that these CNTs coatings have some disorder in their structure. The fitting analysis based on intensity ratio of D to G peak (I_D/I_G ratio) suggest that the CNTs coatings have slightly higher disorder than starting MWCNTs material.

Supplementary Figure S1: Raman spectra of starting MWCNTs recorded in the range of $1200\text{--}3000\text{ cm}^{-1}$ on three different locations namely Loc 1, Loc 2 and Loc 3.

Supplementary Figure S2: (a) Raman spectra of samples CNT-2 and CNT-3. Inset shows a magnified view of the D and G peaks.

Supplementary Information 2

FTIR Analysis: To further examine the bonding environment of CNT coatings, an Fourier transform infrared (FTIR) spectrum of CNT-2 was recorded, Figure S3. The bands at 1048

cm^{-1} and 1155 cm^{-1} are assigned to O–H deformation C–O stretching vibrations, respectively. The peak at 1739 cm^{-1} is attributed to C=O stretching vibrations in the carboxyl group. This indicates the –COOH group functionalization of CNTs, consistent with XPS analysis. Furthermore, the FTIR spectrum shows a peak around 1594 cm^{-1} which corresponds to C=C stretching vibrations. The presence of the peaks at 1441 cm^{-1} , 1662 cm^{-1} and 515 cm^{-1} is due to the N–H stretching, N–H bending and Si–O–Si rocking vibrations, respectively, indicating the functionalization of CNT with N-(2-aminoethyl)-3-aminopropyl-trimethoxysilane which is used as the dispersing agent for the formation of a stable colloidal suspension of CNTs and acts as a binder for the fabrication of integral CNT films on the silicon substrate. Apart from these peaks, various other peaks are also found which however are not the peaks of interest.

Supplementary Figure S3: FTIR spectrum of CNT-2 coating.

Supplementary Information 3

Electrical Transport: In Figure S4, we examine the nonlinearity between devices to determine the turn-on voltage, V_{on} , defined here as the voltage at which the current transitions from linear to non-linear regimes. Figures 4a and 4b (main manuscript) show low- and moderate-

voltage I-V curves to visually the device nonlinearity. We see a decent nonlinearity begin to form at low bias in CNT-1 and CNT-2. The marginal nonlinearity at low bias in an otherwise ohmic regime could be due to presence of contamination at the interface of the probe and the metal contacts, and other artifacts.

Supplementary Figure S4: Electrical characterizations for carrier transport. I-V curves (in linear scale) for different devices plotted in the range of (a) 0-1 V and (b) 0-3 V. The solid lines in (a-b) guide the eye to show the non-linearity. (c) $\log(I)$ - $\log(V)$ curves are plotted to examine the ohmic and non-ohmic regimes, and to estimate the V_{on} , which we define here as the voltage at which the current deviates from linear to non-linear regimes. The solid lines in (c) are shown to highlight the transition from linear to non-linear behaviour.

To quantitatively estimate the turn-on voltage, we plot log-scale I-V curves. Two lines are fit over each curve: the first showing the region with linear behavior (slope ~ 1) and the second

showing significantly nonlinearity (slope >1). Based on the point of interception between the linear and nonlinear fits, the values of V_{on} are estimated to be around 2.5 V in device CNT-1, 1.1 V in CNT-2 and 2.4 V in CNT-3 (with an error of ± 0.5 V or less).