Ink-jet printed semiconducting carbon nanotube ambipolar transistors and inverters with chemical doping technique using polyethyleneimine

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We demonstrate an ink-jet printed ambipolar transistor and inverter based on a semiconducting carbon nanotube (CNT) network as a channel by employing a solution-based chemical doping technique with an amine-rich polyethyleneimine (PEI) polymer. The PEI polymer has been reported as an efficient electron dopant and thus contributes to enhancing n-type conduction in CNT transistors. However, because of the presence of ambient oxygen and moisture and the hygroscopicity of the PEI polymer, their p-type conduction did not seem to be effectively reduced, resulting in rather ambipolar conduction. Therefore, we utilize a simple solution-based doping technique to convert p-type semiconducting CNT transistors into ambipolar transistors and fabricate the ambipolar CNT transistor by combining a cost-effective ink-jet printing technique and a simple spin-coating method. Finally, the electrical performance of the logic inverter consisting of identical two ambipolar CNT transistors is also evaluated and optimized by adjusting the concentration of PEI polymer. *Published by AIP Publishing*. [http://dx.doi.org/10.1063/1.4973360]

Carbon nanotubes (CNTs) have attracted extensive interest for various electronic device applications because of high carrier mobility and current density,[1,2] extremely good mechanical strength,[3] excellent flexibility,[4] and solution-based processability at room temperature.[5] However, CNT-based electronic devices, i.e., CNT transistors, have typically exhibited only p-type characteristics under ambient conditions due to the strong adsorption of environmental oxygen and moisture.[6–8] These characteristics can limit the implementation of conventional concepts for logic circuits utilizing both unipolar p- and n-type transistors in the realization of complementary metal-oxide-semiconductor (CMOS). Thus, numerous methods have been proposed for the control and enhancement of n-type conduction in CNT transistors, including the use of (i) low workfunction metal for source/drain contacts,[9–11] (ii) atomic layer deposited (ALD) high-κ oxide directly on the CNTs,[12,13] and (iii) chemical doping on either the contacts or the bulk of CNTs.[14–16] Additionally, without complex designs involving different n- and p-type unipolar transistors, ambipolar logic circuits (or CMOS-like logic circuits) consisting of identical ambipolar CNT transistors have recently received considerable attention for other methods of efficiently fabricating logic circuits.[17–20] Ambipolar transistors allow both electrons and holes to be injected and transported depending on the bias conditions in a single device. One of the significant advantages of using ambipolar transistors in logic circuits is ease of fabrication, as a single type of transistor can be used rather than spatially complicated patterned and designed unipolar p- and n-type transistors. In addition, it has been reported that ambipolar transistors offer more flexible circuit design options in terms of area, power, and speed. Hence, a variety of circuits composed of ambipolar CNT transistors have been researched, verifying their practical feasibility.[19,20]

Herein, we present ink-jet printed ambipolar transistors based on a pre-separated, semiconducting CNT network as an active channel. Chemical doping with amine-rich polyethyleneimine (PEI) polymer was employed to functionalize the CNTs to produce and verify the ambipolar characteristics. PEI has previously been reported as an efficient electron dopant that exhibits stability in air, and thus, numerous reports have been predominantly focused on the implementation of n-type CNT transistors using PEI polymer.[21–25] However, it was frequently observed that, although the PEI polymer contributes to enhancing n-type conduction in CNT transistors by its electron-donating ability in amine-containing molecules, their p-type conduction did not seem to be effectively reduced even when a high concentration of PEI was utilized, resulting in rather ambipolar conduction with PEI doping. Therefore, using these properties, PEI-functionalized ambipolar CNT transistors acting as either n- or p-type transistors were fabricated by a combination of ink-jet printing and a simple spin-coating method in this work. Then, they were integrated to fabricate a logic inverter, consisting of two identical ambipolar PEI-doped CNT transistors, to explore their electrical performance. By adjusting the concentration of PEI polymer, we could evaluate and optimize the electrical performances of the logic inverters.

Fig. 1(a) presents a schematic illustration of ink-jet printed ambipolar transistors based on a pre-separated, semiconducting CNT network as a channel. The transistors were fabricated on 1.5 cm × 1.5 cm pieces of silicon wafer, highly p-doped as a common back-gate, with a thermally grown 55-nm-thick back-gate oxide (SiO_2) layer. The substrate was first functionalized with a poly-L-lysine solution (0.1% w/v in H_2O, Sigma Aldrich) to form an amine-terminated adhesion layer,[26] which acted as an effective adhesion layer for

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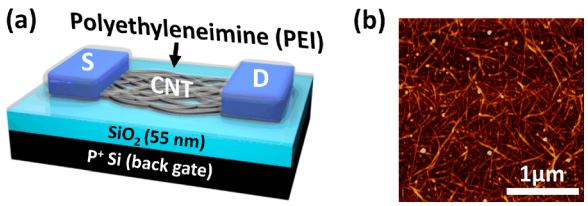

FIG. 1. (a) Schematic illustration of ink-jet printed semiconducting CNT ambipolar transistor. (b) AFM image (2.5 μm × 2.5 μm, z-scale is 10 nm) of the CNT network channel created by the drop-coating method using 90% semiconducting CNT solution.

the deposition of CNTs. The substrate was then thoroughly rinsed with deionized (DI) water and isopropanol. The CNTs, as an active channel material, were deposited by immersion in purified 90% semiconductor-enriched CNT solution (NanoIntegris, Inc.) for several hours, followed by rinsing with DI water and isopropanol and drying with flowing nitrogen. The source and drain electrodes were inkjet-printed with silver (Ag) nanoparticle ink, followed by an annealing process at 150 °C. Next, poly-4-vinylphenol (PVP) was inkjet-printed onto the surface to define the channel widths. The CNTs outside the channel region were then removed by an oxygen plasma-etching step to remove unwanted paths to electrically isolate the devices from one another. Afterward, the PVP was removed with acetone, isopropanol, and flowing nitrogen. We used the branched PEI polymer (average molecular weight: 800, Sigma Aldrich) to produce ambipolar characteristics in the CNT network transistors. First, a typical branched PEI polymer with the chemical formula of $H(NHCH_2CH_2)_nNH_2$ was dissolved in methanol (0.01–50 vol. %) and then dispensed on the top surface of the devices using spin-coating at 500 rpm for 300 s. Next, the baking process was performed at 65 °C to evaporate the methanol. Finally, the remaining PEI on the CNTs was removed by rinsing again with methanol, leaving nearly a monolayer of PEI irreversibly adsorbed on the CNTs.[21–24] From the previous reports, it was observed that roughly a monolayer of PEI was non-uniformly coated on the CNTs at the molecular scale, even though thorough rinsing with solvents was employed. Therefore, we speculated that the PEI layer becomes more uniform and continuous, and denser with increasing the PEI concentration (n_{PEI}). Further in-depth investigation using transmission electron microscopy remains for characterizing the PEI layer on the CNTs. Most of the layers in the devices were fabricated by a cost-effective ink-jet printing technique and simple spin-coating method without the use of physical masks and photolithography. Strictly speaking, the CNT networks were not printed; instead, a solution-based drop-coating process was used to deposit the CNT networks. Although the ink-jet printing process is a more cost-effective approach in terms of CNT usage than the drop-coating process, it was observed that the device yield and uniformity from the drop-coating method were superior to the results of the ink-jet printing process.[27] Fig. 1(b) shows an atomic force microscopy (AFM) image of a typical CNT network constructed from the 90% semiconducting CNT solution. The CNTs were well percolated, and the density of the CNT networks was estimated to be approximately 75–81 CNTs/μm^2.

Fig. 2(a) shows the drastically altered electrical characteristics of CNT transistors after PEI adsorption. The transfer curves, i.e., drain current-gate voltage, I_{DS}–V_{GS}, were measured at a drain to source voltage (V_{DS}) of −0.5 V under ambient conditions. Prior to PEI adsorption, the as-fabricated CNT transistor exhibits p-type FET characteristics due to the adsorption of environmental oxygen and moisture. On the other hand, the transfer curves were significantly altered by increasing the n_{PEI}. Even at a small n_{PEI} of 0.01 vol. %, the n-type current at positive V_{GS} values began to show a clear increase. Furthermore, as the n_{PEI} increased up to 50 vol. %, the conduction type significantly changed from the initial p-type to strong ambipolar conduction, rather than unipolar n-type conduction. These results are highly reproducible with 30 independent CNT transistors. Moreover, extensive rinsing of the devices cannot remove the PEI completely from the CNTs, resulting in irreversible changes in the electrical characteristics.

It is well known that PEI has the electron-donating ability of amine groups in the polymer and contains one of the highest densities of amine groups among all polymers.[21] The amine groups in the PEI polymer were found to be sufficient to cause significant changes in the electrical conductance of CNTs. The strong physisorption and weak chemisorption of the amine molecules on the CNTs causes a shift of the Fermi level toward the conduction band by electron donation.[28] Therefore, it has been predominantly reported that the high density of electron-donating amine functionalities in PEI results in significant unipolar n-doping to a point where the adverse effect of p-doping due to adsorption of the environmental oxygen and moisture is reduced. However, in our case, it should be noted that a significant p-type current was still observed at negative V_{GS} values even when a high

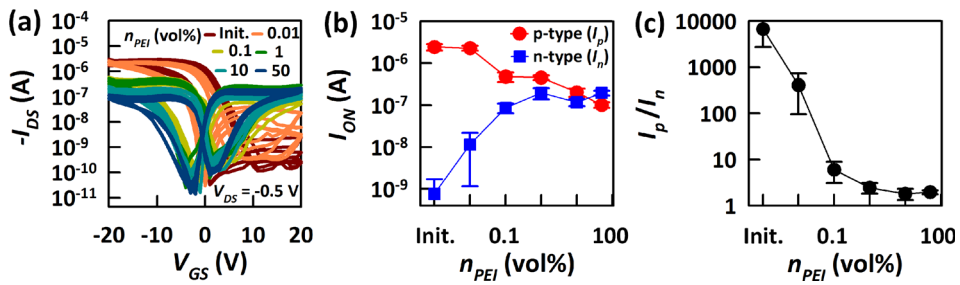

FIG. 2. (a) Transfer characteristics (I_{DS}-V_{GS}) of a total of 30 CNT transistors using various n_{PEI} values with channel lengths (L = 250 μm and 350 μm) and the same width (W = 400 μm). The "Init." in the graph shows the data extracted from the CNT transistor with no PEI doping (i.e., bare CNT network). (b) Plot of extracted I_{ON} and (c) ratio of I_{ON} at p- and n-type conductions (I_p/I_n or I_n/I_p) in PEI-doped CNT transistors with varying n_{PEI}.

n_{PEI} of 50 vol. % was employed. This result is attributed to the measurement under ambient conditions where oxygen and moisture co-existed.[29] Because the PEI polymer most likely absorbs those molecules, i.e., exhibiting hygroscopicity,[29–32] the spontaneous electron transfer from CNTs to those molecules through the intermediate of the redox reaction still occurs, resulting in strong ambipolar conduction.[33,34] The further increase of n_{PEI} leads to degradation of the current on/off ratio because a continuous PEI layer on the device was formed with increasing n_{PEI}, resulting in reduced gate modulation due to the charges accumulated in the PEI polymer. Large and unwanted hysteresis behaviors in the transfer curves can be seen, but it can be further improved by the encapsulation of hydrophobic polymers or dielectrics to close the exposed CNT network.

Fig. 2(b) plots the extracted on-state current s(I_{ON}) for p- and n-type conduction, i.e., I_p and I_n, respectively, in PEI-doped CNT transistors with varying n_{PEI}, measured at V_{GS} of −20 V and 20 V, respectively. Below an n_{PEI} of 1 vol. %, I_n was significantly enhanced, and in contrast, I_p was slightly decreased. The changes in I_n and I_p by PEI adsorption began to be saturated above an n_{PEI} of 1 vol. %, resulting in a well-balanced ratio between them, as shown in Fig. 2(c). The best ambipolarity was obtained at an n_{PEI} of 10 vol. %, with the smallest ratio of I_p/I_n (or I_n/I_p). It is worth noting that the degree of balance in n- and p-type conduction can be controlled simply by the selection of n_{PEI}. The hole and electron mobilities (μ_h and μ_e) for p- and n-type conduction were calculated to be $3.9 \pm 3.6\,cm^2/V{\cdot}s$ and $1.2 \pm 0.8\,cm^2/V{\cdot}s$, respectively, from 25 independent CNT transistors possessing different channel lengths ($L = 250\,\mu m$ and $350\,\mu m$) and the same width ($W = 400\,\mu m$). The highest μ_h and μ_e values we obtained were $15\,cm^2/V{\cdot}s$ and $3\,cm^2/V{\cdot}s$, respectively, using a cylindrical model to calculate the gate capacitance.

To demonstrate the utility of the ambipolar PEI-doped CNT transistors, inverters were produced by combining two identical ambipolar CNT transistors constructed using various n_{PEI} values ranging from 0 to 50 vol. %. Fig. 3(a) presents the voltage transfer characteristics, i.e., output voltage vs input voltage, V_{IN} vs V_{OUT}, of the inverters, measured at a supply voltage (V_{DD}) of 20 V. Both hole and electron carriers of ambipolar CNT transistors in this inverter can be transported, depending on the V_{GS} values. The conduction and valence bands of the CNTs are upshifted to transport hole carriers with a negative V_{GS} value, while the conduction and valence bands of the CNTs are downshifted to transport electron carriers with a positive V_{GS} value. In this inverter

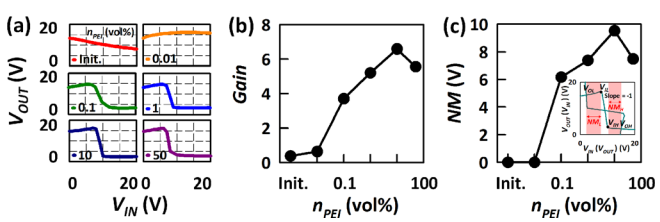

FIG. 3. (a) Voltage transfer characteristics of CMOS-like inverter consisting of two identical ambipolar PEI-doped CNT transistors with varying n_{PEI} at the V_{DD} of 20 V. (b) Voltage gain ($|dV_{OUT}/dV_{IN}|$) and (c) *NM* obtained from voltage transfer curves with varying n_{PEI}. Inset is a plot of *NM* criteria extracted from the voltage transfer curve with n_{PEI} of 10 vol. %.

configuration, the V_{DD} and ground terminals are interchangeable due to the device symmetry. At n_{PEI} values of 0 vol. % and 0.01 vol. %, the inverter did not show the appropriate switching behavior, which is attributed to the insufficient n-type current in the bottom ambipolar transistors. As n_{PEI} was increased to 0.1 vol. %, however, the inverter showed the proper switching of V_{OUT} from high to low values as V_{IN} was swept from low to high values. Further increases of n_{PEI} showed gradually enhanced performance in the inverters because the n- and p-type currents became better balanced. However, V_{OUT} was not constant for both high and low values of V_{IN}, as V_{OUT} increases slightly with V_{IN}. This common feature among this type of inverter arises because one of the two ambipolar transistors is not completely turned off while the other ambipolar transistor is turned on.[35] The voltage gain defined as $|dV_{OUT}/dV_{IN}|$ and the noise margin (*NM*) were also extracted from voltage transfer characteristics, as shown in Figs. 3(b) and 3(c), respectively. The inset in Fig. 3(c) shows the *NM* criteria extracted from the voltage transfer curve with an n_{PEI} of 10 vol. %. *NM* is defined as the sum of the low-state noise margin ($NM_L = V_{IL} - V_{OL}$) and the high-state noise margin ($NM_H = V_{OH} - V_{IH}$). The best inverter performance in terms of the gain and *NM* can be obtained at an n_{PEI} of 10 vol. %, where the n- and p-type currents were the best balanced. At an n_{PEI} of 50 vol. %, the inverter performance was slightly decreased, as the n-type current was higher than the p-type current.

As a series evaluation of the ambipolar inverter, the performances of three different types of inverters, namely, the pseudo p-type MOS (PMOS) inverter consisting of two initial p-type CNT transistors, a CMOS inverter consisting of an initial p-type CNT transistor as the p-type and a PEI-doped CNT transistor as the n-type, and an ambipolar inverter consisting of two PEI-doped CNT transistors, are shown in Fig. 4. The circuit diagrams for each inverter were shown in the inset figure. We only considered the V_{IN} range from 0 to V_{DD} for practical uses. Fig. 4(a) shows the characteristics of the pseudo PMOS inverter, and the bottom initial p-type CNT transistor always operates in the saturation region Therefore, the pull-up operation cannot properly occur, compared to the pull-down operation, so the maximum V_{OUT} cannot reach to the V_{DD} value. The maximum voltage gain is only approximately 1 at a V_{DD} of 10 V. Figs. 4(b) and 4(c) present the characteristics of the CMOS inverter and ambipolar inverter, respectively. We used the n_{PEI} of 50 vol. % for the top transistor in the CMOS inverter because the PEI-doped CNT transistor with an n_{PEI} of 50 vol. % showed the highest n-type current among various n_{PEI} values. Moreover, an n_{PEI} of 10 vol. % was used for two PEI-doped CNT transistors in the ambipolar inverter, due to the most well-balanced properties between the p- and n-type currents. Within the V_{IN} range from 0 to V_{DD}, it was observed that the V_{OUT} cannot be lowered, i.e., did not show the proper pull-down operation because the threshold voltage (V_T) between the initial p-type CNT transistor (−1.8) and PEI-doped CNT transistor (2.1) was significantly mismatched. This result indicates that the additional V_T adjustment is required to match the V_T between the pull-up and pull-down transistors. However, for the pull-up operation, the maximum V_{OUT} value nearly reached the V_{DD} value due to the high p-type current in an initial p-type CNT transistor.

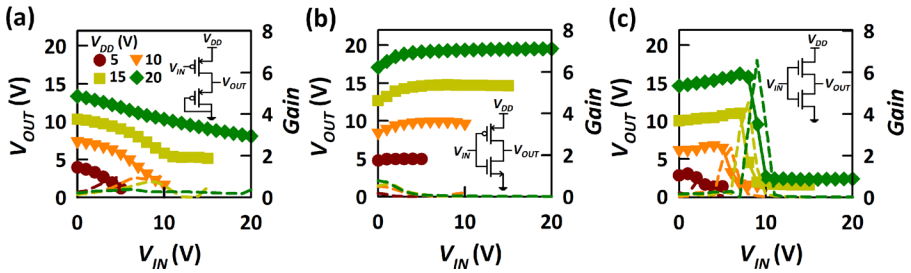

FIG. 4. Inverter performance of three different types, namely, (a) the pseudo PMOS inverter consisting of two initial p-type CNT transistors, (b) the CMOS inverter consisting of an initial p-type CNT transistor as the p-type and a PEI-doped CNT transistor as the n-type, and (c) the ambipolar inverter consisting of two PEI-doped CNT transistors at different V_{DD}.

On the other hand, the ambipolar PEI-doped CNT transistors in the ambipolar inverter can operate as pull-up and pull-down transistors, exhibiting proper logic functionality. The high voltage gain and NM were recorded as approximately 7 and 10, respectively, at a V_{DD} of 20 V.

In conclusion, we demonstrate ink-jet printed ambipolar transistors and inverters based on a semiconducting CNT network as a channel. The CNTs were functionalized by amine-rich PEI polymer as a chemical doping technique to produce the ambipolar characteristics. We confirm that the simple spin coating of PEI polymer facilitates ambipolar transport, rather than unipolar n-type transport, in CNT transistors under ambient conditions. In addition, we could easily optimize the performance of the logic inverters by adjusting n_{PEI}. Although further improvement of the device performance seems to be necessary, through the use of ohmic Pd source/drain electrodes and thinner/high-k gate dielectrics, the concept presented here will play an important role in various future CNT electronics.

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