Nanoscale carbon-nanotube field-effect transistors (CNT-FETs) have been a focus of recent studies in next-generation semiconductor architecture. However, in numerous CNT-FETs that have been proposed, process variations, as well as measurement fluctuations, have occurred regularly, hampering the development of these devices for practical applications. Moreover, it is difficult to control the conduction polarity of individual CNTs. This is particularly challenging in the case of complementary CNT-FETs, where the n- or p-channel of an individual CNT is located on the same chip, although doping is inevitable in the implantation of complementary circuits. The fabrication of a nanoscale gap between a source and a drain has recently attracted considerable attention for electronic devices, molecular devices, and biosensors, but no CNT-FET devices with asymmetric nanogaps have been addressed.

In this study, sub-30-nm complementary doping-free CNT-FETs with polarity control are fabricated in a controlled fashion using DNA molecular lithography. This study demonstrates the polarity control of Schottky barrier (SB) FETs in a sub-30-nm region via source/drain workfunction engineering without complicated chemical doping or structural changes. This technique has many advantages for creating nanoscale high-density devices as well as size-controlled CNT-FETs; it can enable these devices to be operated with polarity control between the n-channel and the p-channel. It is believed that these CNT-FET devices, featuring an asymmetric nanogap, will be useful for implementing complementary CNT-FET circuits with control of the nanogap size and the transport polarity.

A highly productive framework for implementing nanoscale complementary CNT-FETs with polarity control is presented in Figure 1. Initially, 5 nm of silicon oxide was grown on a highly n-doped (PoCl3 doped for 5 min) silicon substrate during thermal oxidation. Then, single-walled carbon nanotubes (SWNTs) were localized on photolithographically specified areas of the substrate. To do that it is necessary to form a fluorocyclotrichlorosilane (FOTS) layer on the areas. Specifically, a photoresist is spun onto the entire wafer and the area where the active channel is to be formed is photolithographically exposed. The whole wafer is then loaded into a vacuum chamber with liquid FOTS source. The liquid FOTS in a crucible is evaporated onto the active channel area, and forms a self-assembled monolayer (SAM). It is tightly bound to the thermal oxide via covalent bonding of the hydroxyl/trichlorosilane interface. Subsequently, the photoresist is removed to complete FOTS patterning. This self-assembled monolayer (SAM) serves to align SWNTs selectively onto a photolithographically defined active area, and operate as an auxiliary gate dielectric on the thermal oxide. Thereafter, SWNTs dispersed in 1,2-dichlorobenzene are spun onto the wafer. The SWNTs are selectively assembled via attractive coulombic interaction with the pre-patterned hydrophobic self-assembled FOTS terminated by a fluoromethyl group (–CF3) (Figure 1A). In order to interconnect self-assembled SWNTs with a nanogap, the Au/Cr double layers are delineated to create a subsequent drain electrode serving as an SB junction with the self-assembled SWNT substrate. By utilizing a conventional photolithography method, the Au/Cr double layers are delineated to create a subsequent drain electrode serving as an SB junction with the self-assembled SWNTs. The double-stranded DNA (dsDNA, 500 nm in 1 M KH2PO4, pH 6.75) with controlled length and thiol-group termination (purchased from Genotech in Daejeon, Korea) are immobilized on the surface of the parent Au/Cr electrodes at room temperature (RT) for 24 h. After incubation, a monolayer of the DNA emerged sideways from the pre-patterned Au/Cr structures due to the self-recognition characteristics of DNA. Excessive DNAs are removed by washing the substrate with 50 mM of phosphate buffer twice for 5 mins. The distance separating this parent electrode from the second electrode is defined by the length-controlled dsDNA. While there have been several reports on molecular lithography based on large molecule SAMs, a newly proposed DNA template for molecular lithography utilizes the small size of the unit oligonucleotides. Thus it can, in principle, facilitate the length modulation of the DNA with molecular precision of 3.4 Å (Figure 1C). The second electrode with different workfunction metals (Au, Al, or Pd) is deposited with a 45-nm thickness onto the substrate by evaporation and defined by a lift-off process (Figure 1D). Finally, the immobilized DNA strands are removed using DNase I (New England Biolabs Inc., Beverly, MA) at 1 µL mL−1 in a 1× reaction buffer.

The SWNTs dispersed in 1,2-dichlorobenzene exhibit strong affinity to hydrophobic FOTS patterns but show minimal adhesion onto bare SiO2 (Figure 2A and B). The measured contact angle on the surface of the FOTS was 118°; the large contact angle suggests strong hydrophobic–hydrophobic interaction with SWNTs (Figure 2A inset).

According to an AFM analysis, the thickness of the FOTS was...
3.1 nm. A SAM on the thermal oxide reduces the gate leakage current density by one order of magnitude from $1 \times 10^{-1}$ to $1.5 \times 10^{-2}\text{A cm}^{-2}$ compared to the bare thermal oxide with 2 V of applied voltage in a control metal–oxide semiconductor (MOS) capacitor made of heavily n-doped silicon substrate and thermally evaporated aluminum as the top electrode (Figure 2C).[19] The capacitance of FOTS and the thermal oxide dielectric was measured using an LCR meter (HP 4284) with a range from 100 kHz to 1 MHz (Figure 2D). A permittivity level of 7.48 for the 3.1-nm-thick FOTS and 3.9 for a silicon dioxide thickness of 5 nm were extracted from the measured capacitance. Hysteresis in the FOTS layer was observed during the capacitance measurement. However, no hysteresis was seen in silicon dioxide; this is indicative of charging of the FOTS layer with electrons during measurement. This can be useful in memory applications with this fabricated device.[24] The trap center and mechanism of the charging effects in FOTS can be further characterized to achieve high-performance self-assembled devices.

A series of images depicting each set of DNA-templated nanogaps are shown in Figure 3(A and B). The oligonucleotides used for the DNA-templated lithography are summarized in Table 1. The estimated lengths of the dsDNA with the sequence used here were principally 13.6-nm with 40-mer and 20.4-nm with 60-mer. However, the size of the nanogap fabricated using as-proposed DNA-templated lithography initially showed scattered values with standard deviation. This variation occurred because dsDNA in buffer solution is not stretched out perfectly and folds severely in the air after drying,[25] resulting in nonuniform distance between electrodes. In order to mitigate this non-uniformity, dsDNA with more rigid polymer behavior than ssDNA was chosen as the immobilization agent. In addition to that, 1 mM mercapto-hexanol treatment after the immobilization of dsDNA in a high-ionic-strength buffer of 1 M KH$_2$PO$_4$ and charge repulsion between long chain dsDNA and gold structure helped stretch out the dsDNA.[25–27]

Imaging at high resolution with scanning electron microscopy (SEM) showed...
line-edge roughness even on the first Au/Cr layer. This also mitigates uniform nanogap fabrication. To have smooth line edges of the first Au/Cr layer, using a lift-off process for making the first Au/Cr layer is preferable to using a dry or wet chemical etch.

To determine the electronic properties of the device, different work-functioned metal electrodes for the source and the drain were used to fabricate complementary CNT-FETs with unipolar characteristics. For self-assembled individual SWNTs with a crossing nanogap, the dipping time for self-

Table 1. Oligonucleotides used for nanogap formation.

<table>
<thead>
<tr>
<th>Oligo name</th>
<th>Length (-mer)</th>
<th>Sequence (5’-3’)</th>
<th>Estimated nanogap [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>23SBfw-40</td>
<td>40</td>
<td>AGTACCGTGGGGAAAGGCG AAAAGACCACCCGCGAGGGG-SH</td>
<td>~13.6</td>
</tr>
<tr>
<td>23SBR-40</td>
<td>40</td>
<td>CCCCTCGCCGCGGTTCTTTT CGGCTTTCCCTACCAGTACT</td>
<td>~13.6</td>
</tr>
<tr>
<td>23SBfw-60</td>
<td>60</td>
<td>AGTACCGTGGGGAAAGGCG AAAAGACCACCCGCGAGGGG AGTGAAAAAAGACCTGAAAC-SH</td>
<td>~20.4</td>
</tr>
<tr>
<td>23SBR-60</td>
<td>60</td>
<td>GTTCAGGTTCTTTTACACT CCCCTCGCCGCGGTTCTTTT CGGCTTTCCCTACACAGTACT</td>
<td>~20.4</td>
</tr>
</tbody>
</table>

Figure 4. Sub-30 nm-gate-length nanotube FET formed by DNA-templated molecular lithography. A) \(I_{DS} - V_{GS}\) transfer curve of the symmetrical SB (Au/Cr for a source and a drain) CNT-FETs. B) \(I_{DS} - V_{DS}\) curves. C) \(I_{DS} - V_{GS}\) transfer curve of the asymmetrical SB (Pd source and Au/Cr drain vs. Al source and Au/Cr drain). The high workfunction of Pd (\(F_{pd} = 5.1\) eV) and the low workfunction of Al (\(F_{al} = 4.1\) eV) were used for the source electrodes, hole reservoir and electron reservoir. The affinity for the source electrode to emit electrons or holes determines the polarity of the channel as either an n or p channel. D) Schematic band diagrams of the asymmetric SB CNT-FETs: The low workfunction of aluminum has a large barrier height for hole conduction and a small barrier height for electron conduction. Additionally, for the high workfunction of palladium, the opposite holds. The solid line presents the bias condition of \(V_{GS} > 0, V_{DS} > 0\) for electron conduction and dotted line presents \(V_{GS} < 0, V_{DS} < 0\) for hole conduction. The asymmetric SB formed by workfunction engineering of the source electrode results in the unipolar transport of highly scaled CNT-FETs and the determination of the channel polarity.
assembly as well as the concentration of the SWNT suspension were both optimized (SEM images of the fabricated CNT-FETs with various nanogap sizes are shown in Figure S1 of Supporting Information). Furthermore, the selective breakdown of metallic SWNTs on self-assembled SWNT film was conducted when necessary.\cite{29} When two conductors without SWNTs were in close proximity to each other, a tunneling current appeared, depending exponentially on the applied bias and the distance between electrodes, resulting in the breakdown of the nanogap, whose length corresponded to 40-mer DNA, at 0.6 V. This relatively small breakdown voltage of the 13.6 nm nanogap originates from the concentrated electric field at the rough surface of the Au/Cr structure and subsequent breakdown through the medium of air, and is not caused by residual DNA or highly conjugated molecules as they were removed using DNase. In order to suppress the tunneling current below the conducting current via SWNTs, the targeted nanogap was 27.2 nm, corresponding to a DNA length of 80-mer.

For all measurements presented in this paper, the source electrode was grounded at RT in air using an Agilent 4156A parameter analyzer. The electrical results of symmetrically (i.e., the same metal for the source and the drain) Au/Cr-contacted SWNTs are initially presented in Figure 4(A and B). The device exhibited an ambipolar transport,\cite{29} which is typical behavior of Schottky-barrier transistors with highly scaled gate oxide. It had an on–off ratio of 10\(^{4}\) and a subthreshold swing of 180 mV per decade. The \(I_{DS}-V_{DS}\) characteristics show a high source–drain contact resistance, resulting in a truncated curve at the saturation region (Figure 4B).\cite{30} This high contact resistance is due to the incomplete activation between the Cr/SWNT interface. Further optimization of the annealing condition, such as rapid thermal annealing or local Joule heating, is required in order to improve the device characteristics.\cite{31,32} A relatively low current of 15 \(\mu\)A per CNT was attained at a high voltage of \(V_{DS}=1\) V with non-optimized Cr/SWNTs contacts (Figure 4B). The drain current was saturated at a high drain bias, implying that backscattered carriers exist due to optical or zone-boundary phonon emissions with a high drain bias.\cite{33}

For the realization of practical complementary CNT-FETs, unipolar transport of the n- or p-channel is inevitable. By utilizing the asymmetric workfunction of the source and the drain, which can be easily implemented in DNA-templated photolithography, an n-channel CNT-FET and a p-channel CNT-FET were fabricated with an aluminum (\(\Phi_{Al}=4.1\) eV) and a palladium (\(\Phi_{pd}=5.1\) eV) source electrode, respectively. Both had a gold/chromium drain electrode (Figure 4C). Positive (+0.3 V) and negative (−0.3 V) drain voltages were applied for the n- and p-channel branches, respectively. The characterized devices showed unipolar transport behavior and excellent OFF-state performance. This p-FET and n-FET behavior of asymmetric SB CNT-FETs without channel doping can be understood in terms of the schematic band diagrams shown in Figure 4D.

The source electrode, serving as a reservoir of charge carriers, was constantly grounded. Depending on the applied bias of the drain and the gate electrode, electrons or holes are injected from the source electrode to the SWNT channel and collected at the drain electrode. By modulating the SB at the source side, the types of injected carriers from the source can be controlled. The low workfunction of aluminum can easily emit electrons while suppressing hole emission. For the high workfunction of palladium, the opposite condition applies. Conceptually, determination of n- or p-channel unipolar transistors relies on the workfunction engineering of the source and the drain SB metal without any channel doping. Moreover, one CNT can be the n- or p-channel simply by swapping the source and drain electrode in the aforementioned asymmetrical work-functioned source and drain.

In summary, large numbers of nanoscale CNT-FETs were fabricated and characterized without the use of sophisticated electron beam lithography tools. The proposed simple DNA-templated nanogap allows for length scaling of SWNT electronics down to 30 nm and implementation of doping-free complementary CNT-FETs. Without any complicated structural change or chemical doping process, the feasibility of sub-30 nm complementary CNT-FETs with polarity control was demonstrated by modulating the SB height between electrode/SWNTs interfaces. Moreover, this simple fabrication technique can easily be applied to other materials for obtaining ultra-miniaturized devices, including nanowires, nanorods, and molecules. Thus, highly scaled devices based on chemically derived nanomaterials can now be fabricated with this new photolithography tool combined with a top-down and bottom-up (DNA-templated molecular lithography) approach.

Keywords:
carbon nanotubes · DNA templating · doping · field-effect transistors · molecular lithography


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