Transfer-Printing of As-Fabricated Carbon Nanotube Devices onto Various Substrates

*Quy Nguyen Thanh, Huiseong Jeong, Jinwoong Kim, J. W. Kevek, Y. H. Ahn, Soonil Lee, Ethan D. Minot, and Ji-Yong Park**

Most nanoelectronic devices are fabricated on rigid, flat, and smooth substrates such as Si/SiO_2, since well-established semiconducting fabrication processes are typically utilized for such devices.[1] However, there has been growing interest in non-conventional substrates such as soft plastic or nonplanar ones for possible applications in flexible, foldable, or implantable electronics.[2,3] For these future applications, it is essential to establish fabrication processes for devices on diverse substrates.

A common approach is first to place the active nanomaterials such as carbon nanotubes (CNTs), graphene, or nanowires on a new substrate,[4] and then to add electrical connections using the same fabrication processes that have been well-developed for conventional substrates such as Si, as long as the target substrate is compatible with the chemical or thermal processes involved.[5,6] An alternative, yet promising approach is to apply all the fabrication steps on a conventional substrate such as Si/SiO_2 and then transfer-print the entire working device onto the target substrates.[7,8] In this way, harsh synthesis and fabrication steps can be avoided on the target substrate. It has been demonstrated that Si devices can be transfer-printed this way with or without sacrificial layers onto various substrates.[2,8] In these cases, however, devices were first fabricated on an elastic elastomer substrate such as polyimide (PI) on top of Si and then transfer was completed by pasting the elastomer substrate on various other substrates with or without an additional adhesive layer first applied on the target substrates.

CNTs are a difficult material to transfer owing to their small diameters (1–3 nm) and strong adhesion to the substrate. Conformal coating of CNTs with a strong adhesion layer such as gold is typically used to transfer CNTs from growth substrates to other substrates.[4,6] So far, most CNT devices on flexible substrates have been fabricated using transferred CNTs (either from the dispersion solution or the growth substrate) followed by fabrication processes on the substrates, which still has limitations associated with process compatibilities. These problems can be circumvented if fabricated CNT devices as a whole can be released and transfer-printed on the target substrates. CNTs (and also graphene) are well suited for this type of process since they are very robust and resistant to harsh chemical processes so that SiO_2 can be easily used as a sacrificial layer without degrading their electrical properties. A similar approach was used before to transfer as-fabricated CNT devices onto flexible substrates that were also used as an adhesive and a holder.[7,9] In these cases, original CNT devices were transferred to the flexible substrates in upside-down configuration.

In this Communication, we report direct transfer-printing of as-fabricated CNT devices onto various non-conventional substrates, in which we can place an exact replica of the original device on a new substrate. CNTs are first thermally grown on a Si/SiO_2 substrate by chemical vapor deposition (CVD) and electrodes are patterned with semiconductor processes. Whole device structures are coated with poly(methyl methacrylate) (PMMA) and then released by etching the sacrificial SiO_2 layer. The devices are then transfer-printed onto nonplanar, soft, or rough substrates with high fidelity by dissolving PMMA. In this way, the Si/SiO_2 substrate which CNTs were contacting in the original devices is replaced by various target substrates. We compared electrical characteristics of the devices before and after the transfer. We also applied the same process to graphene devices successfully. By minimizing processing steps on the target substrates (only mild thermal stress, 80 °C, and exposure to acetone), usable substrates for CNT devices can be greatly diversified.

Figure 1 illustrates our transfer-printing processes. First, a thin layer (~2 µm) of PMMA (solids content 6%, molecular weight 495 kDa) is spin-coated on the CNT devices (Figure 1a) at 500 rpm for 5 s, followed by 2000 rpm for 40 s, then the PMMA layer is hardened at 120 °C for 120 s on the hotplate (Figure 1b). The whole structure is submerged in a buffered oxide etch (BOE) solution at 90 °C for several hours to etch away the sacrificial SiO_2 layer. When etching is complete, the PMMA/CNT-device film is released and floats freely on the surface of the BOE bath (Figure 1c). At this stage, the CNT devices are supported only by the PMMA film and the bottom of the original device is exposed. The PMMA-supported CNT devices are cleaned in a deionized water bath to remove remaining etchant. The PMMA-supported CNT devices are now ready for the transfer-printing procedure (Figure 1d). Thin (a few micrometers) freestanding PMMA films are difficult to handle unless they are kept in a water bath. For the transfer, we put the target substrate into the water bath, underneath the floating

Q. N. Thanh, H. Jeong, J. Kim, Prof. Y. H. Ahn, Prof. S. Lee, Prof. J.-Y. Park
Department of Physics and Division of Energy Systems Research
Ajou University
Suwon 443-749, Republic of Korea
E-mail: jiyong@ajou.ac.kr
J. W. Kevek, Prof. E. D. Minot
Department of Physics
Oregon State University
Corvallis, OR 97331, USA

DOI: 10.1002/adma.201201794

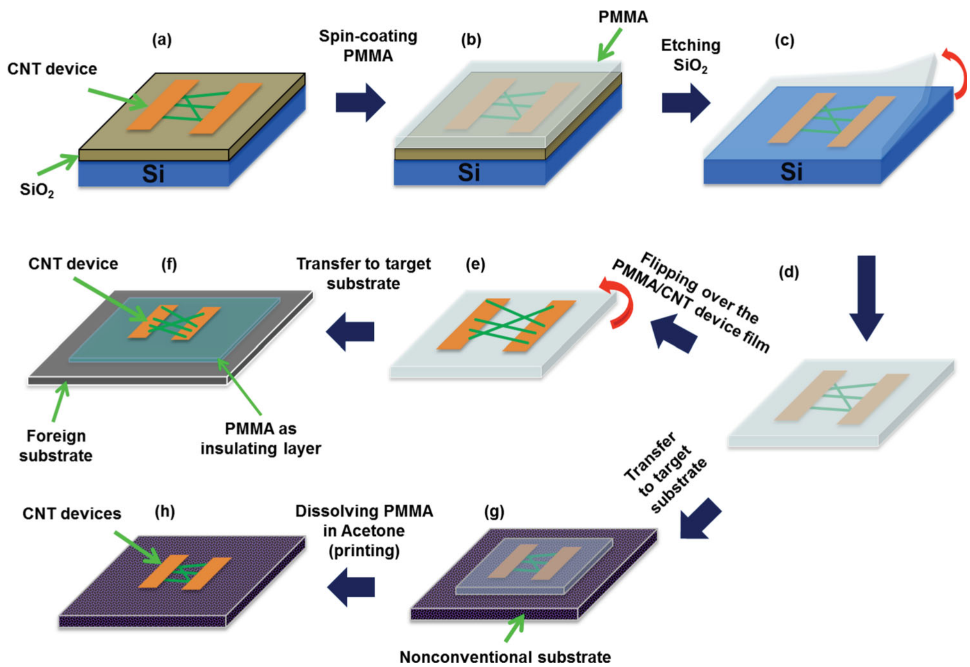

Figure 1. Transfer-printing process flows for CNT devices onto non-conventional substrates: a) the CNT devices are pre-fabricated on a Si/SiO$_2$ substrate, b) PMMA is spin-coated on the device, c) SiO$_2$ is etched in BOE, d) and the PMMA/CNT-device film floats in the water bath. Two paths can be taken from (d). In the first path (e,f), the PMMA/CNT-device film is flipped over as in (e) and placed on a foreign substrate as in (f). In this way, a partially buried CNT device in PMMA film is obtained with a back gate in (f). In the second path, CNT devices are printed on non-conventional substrates: g) PMMA/CNT-device film on a non-conventional substrate. h) CNT devices are printed as PMMA is dissolved in acetone.

PMMA-supported CNT devices, and lift up the film with the substrate. An additional supporting back plane such as thermal tape can be used for easier handling when necessary. We can either use the PMMA/CNT-device film as a stand-alone device or transfer-print it onto a new substrate. In order to use it as a stand-alone device, we flip over the PMMA/CNT-device film (Figure 1e) with device side on top and put it on different substrates, since the film is flexible and conforming (Figure 1f). In this way, the PMMA/CNT-device film can act as a stand-alone device itself with PMMA film as a dielectric layer. For the transfer-printing, the PMMA/CNT-device film is first laid on the target substrate with the device side toward the substrate (Figure 1g). After being dried with N_2 gas, the entire structure is heated in an oven at 80 °C for 1 h to remove trapped water and improve adhesion. Finally, the PMMA film is dissolved in acetone, leaving only the CNT devices on the target substrates (Figure 1h). In this scheme, the original CNT devices are cut and placed on a new substrate, preserving their original device configurations.

We first discuss experiments with the PMMA-supported CNT devices placed on a variety of substrates, which can also act as back gates. We prepared PMMA-supported CNT devices following the process in Figure 1e,f. We first placed them on Al foil and measured the electrical properties, using the Al foil as a back gate. We then peeled off the PMMA-supported devices and placed them on a poly(ethylene terephthalate) (PET) film that had been sprayed with a conducting film of CNTs. We repeated this sequence also on an Al rod (diameter 20 mm), and finally on a Si/SiO$_2$ substrate (thickness of SiO$_2$ is 220 nm), as shown in **Figure 2**a. There were 37 conducting devices in the original chip on Si/SiO$_2$ substrate and all 37 devices were still conducting as measured on the four different substrates. Figure 2b shows the I–V_G characteristics of a representative device when it was on different substrates as in Figure 2a. Compared to the I–V_G characteristics of the pristine device, the PMMA-supported CNT devices show much reduced gate response and almost no hysteresis. Reduced gate response is expected since the dielectric layer (PMMA, a few micrometers thick, dielectric constant ~2.6) is much thicker than the original SiO$_2$ (220 nm thick) dielectric. Gate capacitance varies as $1/\ln(4t_{\text{dielectric}}/d)$, where $t_{\text{dielectric}}$ is the thickness of the dielectric and d is the diameter of a CNT. Therefore, a roughly 3–4 times smaller gate response is expected. However, current levels are mostly comparable and sometimes even a higher current is observed, which indicates that good electrical contacts are maintained. On the other hand, hysteresis almost completely disappears for the PMMA-supported CNT devices, probably due to either the hydrophobic PMMA surface reducing the effects of water[10] or the charge-trapping characteristics of PMMA differing from those of SiO$_2$.[11] Results presented in Figure 2 demonstrate that CNT devices detached from the original growth and fabrication substrate as described in this Communication can still maintain their electrical characteristics, indicating that electrical contacts between CNTs and metal electrodes are preserved.

After cycling the PMMA-supported CNT devices through different substrates as in Figure 2, we transfer-printed the CNT devices by laying the PMMA/CNT-device film on a new Si/SiO$_2$ substrate with device side down and dissolving PMMA with acetone, following the procedure in Figures 1g and h. We

Adv. Mater. 2012,
DOI: 10.1002/adma.201201794

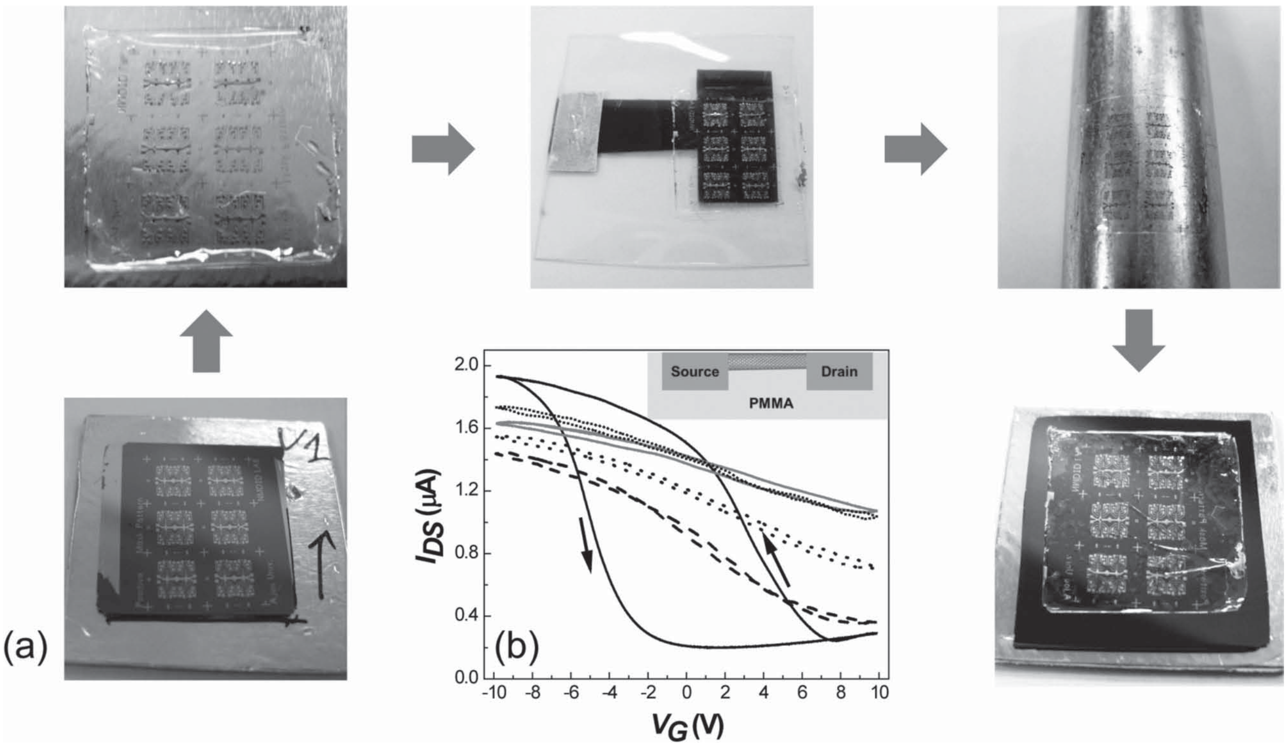

Figure 2. a) CNT devices fabricated on a Si/SiO_2 substrate are released from the substrate following the process in Figure 1. The PMMA/CNT-device film is flipped over and placed on an Al foil, a CNT-sprayed PET film, an Al rod (diameter 20 mm), and a Si/SiO_2 substrate successively (clockwise from left). b) I–V_G characteristics of a representative device as it is placed on the different substrates in (a) (black line: original Si/SiO_2, gray line: Al foil, closely dotted line: CNT-sprayed PET film, dotted line: Al rod, dashed line: new Si/SiO_2). Arrows indicate the direction of the gate sweep. Bias was 100 mV. Inset: Schematic of a CNT device embedded in the PMMA film.

present one example of such CNT devices in **Figure 3**. The optical image in Figure 3a clearly shows that patterns of six (whole pattern size is ~20 mm × 10 mm) are transferred. The atomic force microscopy (AFM) images of one of the devices in the as-fabricated sample (Figure 3c) and the same device in the printed sample (Figure 3d) show that the electrodes and CNTs are transferred with high fidelity. All the CNTs in the original devices can be accounted for in the transferred device. Some PMMA residues remain on the printed devices, which may be cleaned further by prolonged dipping in acetone. For this particular process, 28 out of 37 conducting devices in the original sample survived the transfer. The less perfect transfer yield in this case is probably due to mechanical damage during successive transfer onto different substrates, as in Figure 2a. We obtained almost 100% transfer yield when we directly transferred print devices, as explained below. More examples of the same process are presented in the Supporting Information (Figures S1 and S2). Also the I–V_G characteristics of some devices before and after the process show almost the same characteristics in terms of on/off state current, hysteresis, and transconductance as in Figure 3b. In many cases, the I–V_G characteristics of CNT devices are believed to be significantly affected not only by the intrinsic CNT properties but also by the properties of the substrate, such as surface states or charge traps in SiO_2.[12] However, the result in Figure 3b indicates that the observed device characteristics may be mostly intrinsic to this device and no significant substrate effect is playing a role here. More data from the same process are presented in Figure S3 (Supporting Information).

After confirming that we could transfer-print CNT devices with high fidelity, we tried various non-conventional substrates as target substrates. Some results are presented in **Figure 4**. Identical transfer-printing processes as explained in Figure 1 were used for all the results in Figure 4 and in the Supporting Information. First, we chose rigid substrates such as glass. We were able to transfer-print CNT devices on both planar and nonplanar glass substrates, as shown in Figures 4a and b. The PMMA/CNT-device film is flexible and conforming so that it can be easily placed on the cylindrical surface of a glass vial (with diameter 20 mm) as shown in Figure 4b. Since there was no back gate in the case of glass substrates, we compared I–V_{DS} characteristics of devices before and after the process. They show almost the same I–V characteristics as those measured at zero gate voltage in the original devices, as shown in Figures 4a and b. The transfer yield in both cases was 100%. Next, we applied the same method to flexible plastic substrates. We tried both PET and poly(ethylene naphthalate) (PEN) substrates; results for the PET and PEN substrates are shown in Figure 4c and Figure S4 (Supporting Information), respectively. Both substrates suffer little damage after short (~5 min) dipping in acetone solution to remove PMMA. These substrates are rougher than SiO_2 or glass substrates so that the transfer is more challenging (see Figure S6, Supporting Information). As shown in Figure 4c, the process also works for these substrates.

The transfer yield in these cases was also 100%. However, the resistance of the device is typically 2–3 times that of the original device, as shown in Figure 4c and Figure S5c (Supporting Information).

We also tried more challenging substrates for the process. Different kinds of paper substrates were tried with success. We followed the same procedures to print CNT devices on paper substrates as shown in Figure 4d. We could not dip the whole substrates in acetone solution as in the other cases, but had to remove PMMA step by step by partial dipping or using acetone drops. Photographic paper worked as a target substrate. Unlike the other reported cases, no adhesive layer was used, but the CNT devices were directly printed on the photographic paper in Figure 4d. All the transferred CNT devices still show conduction on this substrate. As shown in AFM images of the transferred devices on these substrates (Supporting Information, Figure S6d), the surface is even rougher than on the plastic substrates, but the transfer still works. Applying device fabrication processes directly on these kinds of substrates is very difficult, and high-temperature growth of CNTs on these substrates would be impossible. Therefore, transfer-printing of the whole device structures, as demonstrated here, is a very effective strategy. I–V_{DS} characteristics of transferred CNT devices on paper substrates show much

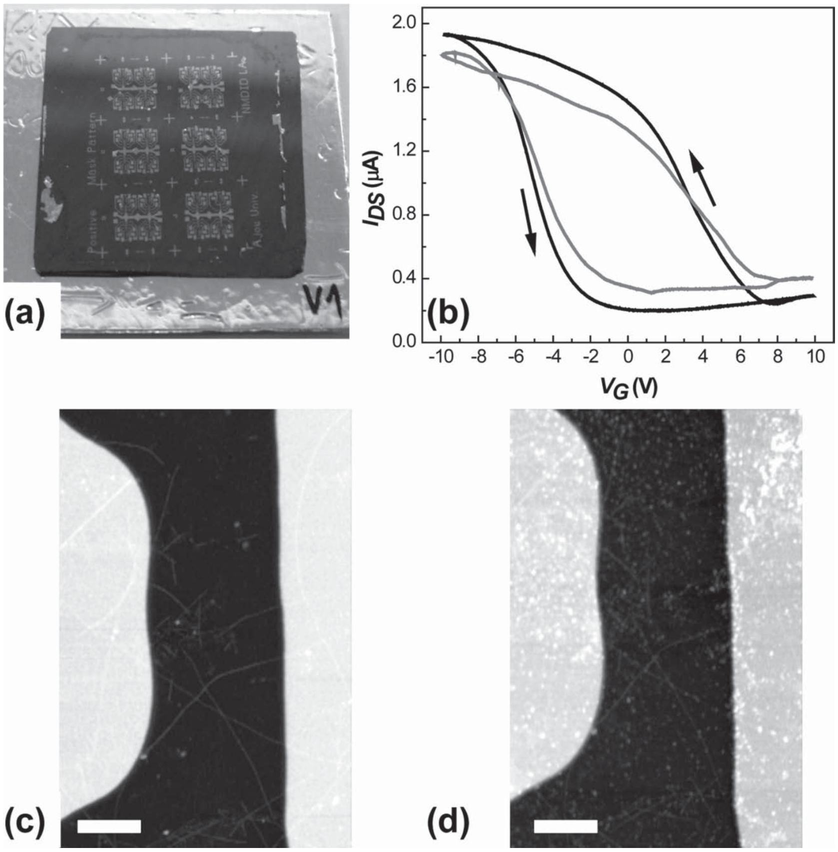

Figure 3. a) Optical image of the printed CNT devices on Si/SiO_2. (The original chip is shown in Figure 2a.) b) I–V_G characteristics of a CNT device before (black) and after (gray) the printing process. Bias was 100 mV. Arrows indicate the direction of the gate sweep. c) AFM topographic image of the original device with the I–V_G characteristic shown in (b). d) AFM image of the same device after the process as in (a). Scale barsrepresent 1 μm.

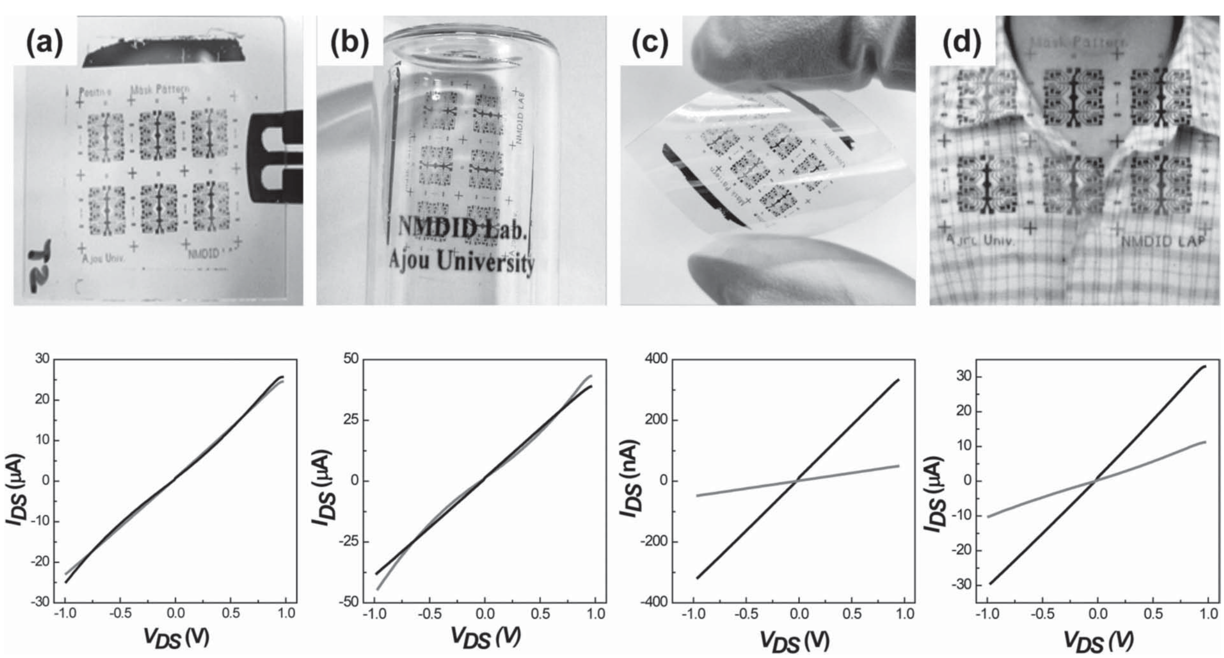

Figure 4. Examples of CNT devices and representative I–V_{DS} characteristics before (black) and after (gray) the transfer-printing to a) a cover glass (planar), b) a glass vial (diameter 20 mm), c) a PET substrate (flexible), and d)photographic paper.

Adv. Mater. 2012, DOI: 10.1002/adma.201201794

reduced currents, as shown in Figure 4d and Figure S5d, similar to plastic substrate cases.

A more statistical representation of the results in terms of conductance changes after transfer-printing on different substrates is presented in Figure S5 (Supporting Information). Generally, conductance was reduced more on rough substrates such as plastic and paper. Since these substrates are rough, some CNTs may got lost or electrodes may not make intimate contact with the target substrate. Another possibility is that the surface condition of these substrates is quite different from the SiO_2 case. Therefore, CNTs may be in a very different electrostatic environment with different effective gate electric field. Since these devices originally exhibited quite strong gate responses, a different effective gate state can result in a quite different resistance. In any case, we have shown that working CNT devices can be placed on these very difficult substrates, significantly extending the range of usable substrates for CNT devices.

We can also apply various surface functionalizations on a target substrate to control the characteristics of a printed device. As an example, we investigated the effect of pre-treating a Si/SiO_2 target substrate in a dilute (2%) HF solution for 20 s. This process is known to make the SiO_2 surface hydrophilic.[13] We found that CNT devices show a marked increase in on-state current when the SiO_2 surface is pre-treated in this way, as shown in **Figure 5**. The increase in the on-state current is associated with better electrical contacts between CNTs and metal electrodes. The more uniform hydrophilic surface arising from the pre-treatment in this case may make more intimate contacts owing to the capillary force between the CNT devices and the new substrate. Another possibility is that the effective doping of CNT, especially at the CNT–electrode contacts due to extra negative charges on the target surface, can improve the contacts. On the other hand, the increased hysteresis as in Figure 5 may be due to more water adsorption on the surface, as previously reported.[10]

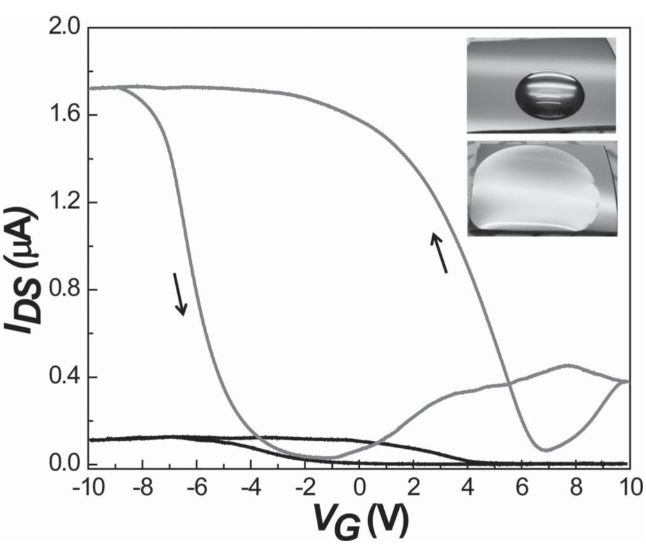

Figure 5. Representative I–V_G characteristics of a CNT device before (black) and after (gray) the transfer-printing process onto a different hydrophilic Si/SiO_2 substrate. Bias was 100 mV. Arrows indicate the direction of the gate sweep. Insets: Water droplet on the new SiO_2 surface before (upper picture) and after (lower picture) being dipped in a dilute (2%) HF solution for 20 s.

As another example of transfer-printing of whole devices, we also applied the same process to graphene devices. Graphene, which is grown by CVD, usually requires elastomer-supported transfer steps onto device substrates.[14] Instead we first fabricated graphene devices using transferred graphene on a Si/SiO_2 substrate, then transfer-printed graphene devices on a new Si/SiO_2 substrate according to the same transfer process as for CNT devices. The results are presented in Figure S7 (Supporting Information). Compared to CNT devices, an overall decrease in current levels is observed for the graphene case. As graphene is a two-dimensional material, it may be more difficult to maintain good electrical contacts during the transfer, compared to CNTs. We found that we could improve the electrical contacts of transfer-printed graphene devices by post annealing.

We believe that good adhesion between electrodes and CNTs is essential for successful and reproducible transfer-printing of CNT devices. The advantage of transferring the whole devices is that intimate contacts between CNTs and electrodes are already made on the smooth SiO_2 substrates as CNTs are partially buried in the electrodes. Therefore, good electrical contacts even on rough substrates are expected to be maintained, as demonstrated for different substrates in this study. Also active CNTs, as they are connected to electrodes, have a better chance of surviving the transfer process as a whole.

In conclusion, we have shown that CNT devices can be easily prepared on various non-conventional substrates such as non-planar glass, flexible plastic, and paper substrates by transfer-printing of whole device structures. In this way, a replica of the original CNT device can be prepared on a new substrate. A simple release-and-transfer scheme works very well for CNT devices and it was found that electrical characteristics of the devices are well preserved for many target substrates. By separating the growth of CNT and the device fabrication processes from the target device substrates, the usable substrates for CNT devices can be greatly diversified. We believe that this technique can also provide a platform for studying interactions between CNTs and various surfaces and their role in the device characteristics.

Experimental Section

Growth of carbon nanotubes: The CNTs used for this study were grown from randomly dispersed Fe catalysts by CVD. Highly doped Si (p-type, < 0.005 Ω cm) with a 220 nm-thick SiO_2 layer was used as a substrate for the growth and subsequent device fabrication. We deposited Fe catalysts by dipping the substrates in $Fe(NO)_3 \cdot 9H_2O$ in isopropyl alcohol (IPA) solution. Afterwards CNTs were grown by CVD at 800 °C under the gas flows of 6 sccm C_2H_4, 200 sccm H_2, and 800 sccm Ar.

Device fabrication: A typical photolithography process with bilayer photoresist was used to pattern the source and drain electrodes with a gap size of 2–8 μm. Electrodes were formed by e-beam evaporation of Ti (1.5 nm thick) and Au (30 nm thick), followed by lift-off. Six identical patterns (pattern size: 4 mm × 4 mm) with 36 electrode pairs were fabricated in one batch.

Device characterizations: We used AFM to examine topographic features of the devices during process flows. I–V characteristics of the devices were obtained under ambient conditions with voltage sources and a current amplifier. For the electrical characterizations, we usually measured source–drain current vs. gate voltage (I–V_G) or source–drain current vs. bias voltage (I–V_{DS}) characteristics of the as-fabricated CNT devices on Si/SiO_2 substrates with Si as a back gate and compared them after the devices had been transferred. Sample preparation and device fabrication procedures for graphene devices are reported in the Supporting Information.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This work was supported by Basic Science Research Program (2011-0003401), Nano R&D Program, Priority Research Centers Program (2011-0030745) through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology and the Excellence Research Program at Ajou University.

Received: May 3, 2012
Published online:

[1] a) O. Hayden, R. Agarwal, W. Lu, *Nano Today* **2008**, *3*, 12; b) O. Auciello, P. Avouris, C. Berger, J. E. Butler, R. W. Carpick, W. A. De Heer, P. N. First, M. S. Fuhrer, M. C. Hersam, C. N. Lau, J. Liu, A. H. MacDonald, R. Martel, J. S. Moon, T. Seyller, J. A. Stroscio, S. Srinivasan, A. V. Sumant, *MRS Bull.* **2010**, *35*, 273.

[2] D.-H. Kim, J. Xiao, J. Song, Y. Huang, J. A. Rogers, *Adv. Mater.* **2010**, *22*, 2108.

[3] a) J. A. Rogers, T. Someya, Y. Huang, *Science* **2010**, *327*, 1603; b) D. H. Kim, N. Lu, R. Ma, Y. S. Kim, R. H. Kim, S. Wang, J. Wu, S. M. Won, H. Tao, A. Islam, K. J. Yu, T. I. Kim, R. Chowdhury, M. Ying, L. Xu, M. Li, H. J. Chung, H. Keum, M. McCormick, P. Liu, Y. W. Zhang, F. G. Omenetto, Y. Huang, T. Coleman, J. A. Rogers, *Science* **2011**, *333*, 838; c) J. Sun, B. Zhang, H. E. Katz, *Adv. Funct. Mater.* **2011**, *21*, 29.

[4] a) S.-H. Hur, O. O. Park, J. A. Rogers, *Appl. Phys. Lett.* **2005**, *86*, 243502; b) S. J. Kang, C. Kocabas, H.-S. Kim, Q. Cao, M. A. Meitl, D.-Y. Khang, J. A. Rogers, *Nano Lett.* **2007**, *7*, 3343.

[5] a) M. A. Meitl, Y. Zhou, A. Gaur, S. Jeon, M. L. Usrey, M. S. Strano, J. A. Rogers, *Nano Lett.* **2004**, *4*, 1643; b) K. J. Lee, M. J. Motala, M. A. Meitl, W. R. Childs, E. Menard, A. K. Shim, J. A. Rogers, R. G. Nuzzo, *Adv. Mater.* **2005**, *17*, 2332; c) D.-m. Sun, M. Y. Timmermans, Y. Tian, A. G. Nasibulin, E. I. Kauppinen, S. Kishimoto, T. Mizutani, Y. Ohno, *Nat.Nanotechnol.* **2011**, *6*, 156.

[6] F. N. Ishikawa, H.-k. Chang, K. Ryu, P.-c. Chen, A. Badmaev, L. Gomez De Arco, G. Shen, C. Zhou, *ACS Nano* **2008**, *3*, 73.

[7] Q. Cao, H.-s. Kim, N. Pimparkar, J. P. Kulkarni, C. Wang, M. Shim, K. Roy, M. A. Alam, J. A. Rogers, *Nature* **2008**, *454*, 495.

[8] a) H.-J. Chung, T.-i. Kim, H.-S. Kim, S. A. Wells, S. Jo, N. Ahmed, Y. H. Jung, S. M. Won, C. A. Bower, J. A. Rogers, *Adv. Funct. Mater.* **2011**, *21*, 3029; b) C. H. Lee, D. R. Kim, X. Zheng, *Nano Lett.* **2011**, *11*, 3435.

[9] K. Bradley, J.-C. P. Gabriel, G. Grüner, *Nano Lett.* **2003**, *3*, 1353.

[10] W. Kim, A. Javey, O. Vermesh, Q. Wang, Y. Li, H. Dai, *Nano Lett.* **2003**, *3*, 193.

[11] a) M. S. Fuhrer, B. M. Kim, T. Dürkop, T. Brintlinger, *Nano Lett.* **2002**, *2*, 755; b) M. Radosavljević, M. Freitag, K. V. Thadani, A. T. Johnson, *Nano Lett.* **2002**, *2*, 761; c) J. S. Lee, S. Ryu, K. Yoo, I. S. Choi, W. S. Yun, J. Kim, *J. Phys. Chem. C* **2007**, *111*, 12504.

[12] L. Prisbrey, T. DeBorde, J.-Y. Park, E. D. Minot, *Appl. Phys. Lett.* **2011**, *99*, 053125.

[13] X. Liang, B. A. Sperling, I. Calizo, G. Cheng, C. A. Hacker, Q. Zhang, Y. Obeng, K. Yan, H. Peng, Q. Li, X. Zhu, H. Yuan, A. R. Hight Walker, Z. Liu, L.-m. Peng, C. A. Richter, *ACS Nano* **2011**, *5*, 9144.

[14] a) A. Reina, X. Jia, J. Ho, D. Nezich, H. Son, V. Bulovic, M. S. Dresselhaus, J. Kong, *Nano Lett.* **2008**, *9*, 30; b) K. S. Kim, Y. Zhao, H. Jang, S. Y. Lee, J. M. Kim, K. S. Kim, J.-H. Ahn, P. Kim, J.-Y. Choi, B. H. Hong, *Nature* **2009**, *457*, 706; c) X. Li, W. Cai, J. An, S. Kim, J. Nah, D. Yang, R. Piner, A. Velamakanni, I. Jung, E. Tutuc, S. K. Banerjee, L. Colombo, R. S. Ruoff, *Science* **2009**, *324*, 1312.

DOI: 10.1002/adma.201201794