Direct printing of aligned carbon nanotube patterns for high-performance thin film devices

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The aligned assembly of carbon nanotubes (CNTs) on substrate presents a significant bottleneck in the fabrication of high-performance thin film devices. Here, we report a direct printing method to prepare laterally aligned thick CNT patterns over large surface regions. In this method, CNT forests were grown selectively on specific regions of one substrate, and the forest patterns were transferred on another SiO2 substrate in a laterally aligned formation while keeping their original shapes. The degree of alignment was characterized via electrical measurement and polarized Raman spectroscopy. Furthermore, we demonstrated high-performance field-effect transistors and gas sensors using our method. © 2009 American Institute of Physics. [DOI: 10.1063/1.3073748]

Thin film devices based on single-walled carbon nanotube (swCNT) were extensively studied for various applications.1-5 Previous successful assembly methods for such devices included selective growth, surface-programed assembly, direct transfer, etc.6-17 However, previous methods usually allowed us to prepare monolayer patterns of swCNTs, and it is still considered to be very difficult to prepare multiple layer of laterally aligned swCNTs. Here, we report a method to directly print laterally aligned thick CNT patterns over large surface area on solid substrates. In this process, swCNTs were grown vertically on specific regions of one substrate, and the vertically grown swCNT patterns were transferred onto another SiO2 substrate in a laterally aligned formation while keeping their original shapes. As a proof of concepts, we demonstrated high-performance field-effect transistors (FETs) and gas sensors using our method.

Figure 1 depicts our assembly method. The first step comprises the patterning of catalyst films for selective swCNT growth [Fig. 1(a)]. Here, aluminum thin films (20 nm) were deposited on glass wafer by thermal evaporation and oxidized at 600 °C in air to form alumina film.18 Then, Fe films (~0.5 nm) were deposited via e-beam evaporation and thermally oxidized at 600 °C for 10 min in air. The photoreisit was patterned on the film by photolithography, and the exposed area of the film was etched by buffered oxide etching process to prepare the catalyst patterns [Fig. 1(a)]. Then, swCNTs were grown vertically on the catalyst patterns using a homebuilt radio-frequency remote-plasma chemical vapor deposition system with water vapor [Fig. 1(b)].18,19 The substrate with vertically grown swCNT patterns (donor substrate) was faced down against a SiO2 substrate (acceptor substrate) and slid ~1 mm to a certain direction with ~5 kPa of downward pressure [Figs. 1(c) and 1(d)]. During the printing process, swCNTs were transferred to the SiO2 substrate with the alignment along the sliding direction, forming laterally aligned thick swCNT film patterns [Fig. 1(e)]. Since the swCNT films form a stable structure, we can continue the microfabrication process to build additional device structures such as electrodes (30 nm Au on 10 nm Ti) [Fig. 1(f)].

Figures 2(a) and 2(b) show the donor and acceptor substrates, respectively. Note that the transferred swCNT patterns on the acceptor substrate maintained their original pattern shapes [Fig. 2(b)]. The linewidth of printed CNT film was larger than that of the CNT forest patterns by only ~5%. When we used the swCNT forest patterns with ~10 μm height, we achieved printed CNT film with ~3 μm thickness, indicating that the angle between the printed swCNTs

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and the substrate was $\sim 17.5^\circ$. The energy-dispersive x-ray spectroscopy on the printed swCNT patterns exhibited minor Al trace ($\sim 1\%$) (Fig. S1 in the supplemental material), implying that some of the detached CNTs were decorated with FeO$_x$/AlO$_x$ catalyst. However, the donor substrate still retained the majority of the catalytic film so that we could reuse the donor substrate for additional swCNT growth after printing. We could also achieve similar dot shaped swCNT patterns [Figs. 2(c) and 2(d)]. The printed pattern width in the perpendicular direction to the sliding was increased by $\sim 1.5$ $\mu$m due to the spreading by downwinding pressure, and that in the parallel direction was decreased by $\sim 0.5$ $\mu$m by compressive stacking.

The printed swCNT films exhibited highly anisotropic electrical properties due to the lateral alignment of swCNTs. We printed cross shaped swCNT patterns and measured the directional resistance values, revealing the anisotropic electrical properties of the printed swCNT films [Fig. 3(a)].

We utilized polarized Raman method to further characterize the CNT alignment in the printed film. At first, we took the Raman spectra using 514.5 nm line from an Ar laser as the excitation light source in two polarization configurations, where both the incident and the scattered photons were polarized parallel (blue curve) or normal (red curve) to the line-pattern direction [Fig. 3(b)]. According to the Raman scattering selection rule, the Raman scattering intensity $I$ from an individual CNT depends on the polarization angle of the light as $I \sim \cos^4 \theta$, where $\theta$ represents the angle between the polarization of light and the alignment of the CNT. Our results show that the G-band ($\sim 1590$ cm$^{-1}$) intensity by the light polarized parallel ($I_p$) to the CNT direction is $\sim 3.7$ times larger than that by the light polarized normal ($I_n$) to the CNTs, indicating a high-degree alignment of CNTs along the sliding direction.

For detailed analysis, we measured polarized Raman spectra using the light with several polarization directions [Fig. 3(c)]. Here, the G-band intensity by the light with a specific polarization direction was normalized to that for the parallel polarization configuration ($\theta=0$). The angular distribution of CNTs in the printed structures was estimated from the normalized G-band intensity data via a simple calculation after assuming that the Gaussian angular distribution of CNTs and the Raman intensity relation $I \sim \cos^4 \theta$ for individual CNTs in the printed structure [Fig. 3(d)]. The results indicate Gaussian angular distribution of CNTs with full width at half maximum $\sim 48^\circ$.

In some applications such as sensors, it is desirable to prepare a single layer of swCNTs [Fig. 4(a)]. We placed the printed swCNTs in $o$-dichlorobenzene and applied ultrasonic vibration with 30 W power for 5 s to remove most of swCNTs and prepare swCNT monolayer. In $o$-dichlorobenzene, the adhesion forces between swCNTs and SiO$_2$ surface were stronger than those between swCNTs and AlO$_x$ catalyst. However, the donor substrate still retained the majority of the catalytic film so that we could reuse the donor substrate for additional swCNT growth after printing. We could also achieve similar dot shaped swCNT patterns [Figs. 2(c) and 2(d)]. The printed pattern width in the perpendicular direction to the sliding was increased by $\sim 1.5$ $\mu$m due to the spreading by downwinding pressure, and that in the parallel direction was decreased by $\sim 0.5$ $\mu$m by compressive stacking.

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experiments show that rather long swCNTs (\(\sim 10 \, \mu \text{m} \) long) were easily broken into small pieces (\(\sim 2 \, \mu \text{m} \) long) by ultrasonic treatment. However the breaking process slowed down after the fragmentation of the long swCNTs. Thus, we could still build various devices such as FETs and sensors using this process.

We demonstrated the high-performance FETs based on the swCNT monolayer patterns [Fig. 4(b) and Fig. S3 in the supplemental material].\(^{20}\) Since our swCNT networks include metallic swCNTs, some metallic paths in the network may result in poor on-off ratio. To achieve high-performance FETs with a large on-off ratio, the density of swCNT networks was lowered down to a single monolayer by ultrasonic treatment.\(^{27,28}\) When the swCNT density in the swCNT network was low, it was more likely that only semiconducting paths were formed because there were usually more semiconducting metallic paths in the network.

Our gas sensors exhibit gas sensitivity using monolayer films of swCNTs.\(^{28}\) Our gas sensors were fabricated by printing laterally aligned thick and monolayer swCNT films and print laterally aligned thick and monolayer swCNT films and should open up various device applications based on swCNTs.

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\(^{20}\) See EPAPS Document No. E-APPLAB-94-038904 for supplementary experimental data. For more information on EPAPS, see http://www.aip.org/pubservs/epaps.html.


