

Spatially Selective Guided Growth of High-Coverage Arrays and Random Networks of Single-Walled Carbon Nanotubes and Their Integration into Electronic Devices

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Thin films of single-walled carbon nanotubes (SWNTs) can provide semiconducting and/or conducting components of passive and active (e.g., transistors) electronic devices.¹ Potential applications range from large-area, mechanically flexible systems, where semiconducting SWNT films could provide advantages over conventional small-molecule or polymer semiconductors, to high-performance devices, where they could provide alternatives to large-grained polysilicon or even single-crystal silicon. For the former class of application, random networks of SWNT might offer sufficient performance. For the latter, densely packed aligned arrays of SWNT are preferred. Forming such arrays, patterning their coverage, and, possibly, interfacing them with SWNT networks represent significant experimental challenges. Modest degrees of alignment and coverage can be achieved by controlled deposition of SWNTs from solution suspensions^{2,3} or by specialized growth methods.^{4,5} A new technique for generating arrays uses chemical vapor deposition (CVD) of SWNTs on single-crystal substrates of sapphire^{6,7} or quartz.⁸ Optimized CVD growth on quartz can yield well-aligned arrays over large areas and with coverages up to 1 SWNT/ μm . The coverage can be increased beyond this level, but only at the expense of degraded alignment, due possibly to detrimental effects of interactions between growing SWNTs and unreacted catalyst particles. We report here a method that avoids these problems by spatially patterning the catalyst. The strategy yields perfectly aligned, high-coverage arrays of SWNTs in well-defined geometries; it can also, in the same growth step, produce dense, random networks of SWNTs self-aligned and electrically interfaced to these arrays. The geometries of these SWNT films enable their easy integration into high-performance, planar devices.

Figure 1 illustrates the experimental approach. The substrates were ST-cut quartz obtained from Hoffman Materials Inc. and subsequently annealed for 8 h at 900 °C in air. Deep ultraviolet photolithography defined openings (e.g., two square regions as shown in Figure 1) in 400-nm-thick poly(methyl methacrylate) (PMMA) photoresist (MicroChem, 495PMMA). Spin-casting ferritin diluted 1:20 (v/v) with deionized (DI) water deposited catalyst on the PMMA and the exposed regions of the quartz. Washing with acetone, isopropyl alcohol, and DI water removed the PMMA and produced a bare quartz substrate with catalyst located in regions corresponding to the patterned openings in the PMMA. The ferritin was sufficiently well adhered to the quartz that most or all of it remained during the steps to remove the PMMA. The deposition conditions (i.e., catalyst concentrations and spin speeds) defined the number of catalyst per unit area in these regions. (There is some nonuniformity in the distribution of catalyst particles within the patterned regions.) Heating the substrate at 900 °C for 10 min oxidized the catalyst. Cooling to room temperature and then heating to 900 °C in a hydrogen environment reduced the catalyst. Purging

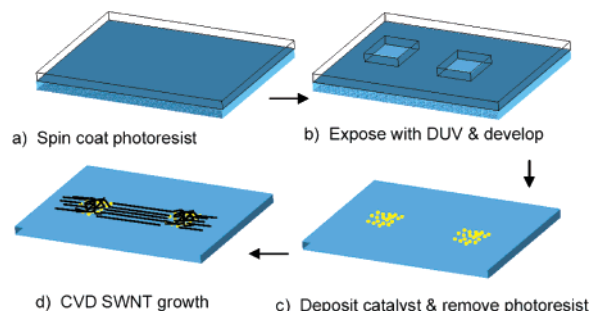


Figure 1. Schematic illustration of the steps for generating self-aligned patterns of dense arrays and random networks of single-walled carbon nanotubes. The approach uses CVD growth on ST cut single-crystal quartz with patterned ferritin catalyst. Preferential growth direction is along the $[2-1-10]$ crystallographic direction.

with hydrogen at 900 °C for 1 min and then introducing a flow of methane (2500 standard cubic centimeters per minute (sccm)) and hydrogen (75 sccm) at 900 °C for 10 min led to the growth of SWNTs. High-density random networks of SWNTs formed in the regions of the catalyst, which is present at high coverage for the cases examined here. Nearly perfectly aligned SWNT emerged from these regions along directions of preferred growth on the quartz, as illustrated schematically in Figure 1 and described in more detail below. Preferential growth direction is along the $[2-1-10]$ crystallographic direction of single-crystal quartz.⁸

Figure 2 presents scanning electron and atomic force micrographs (SEMs and AFMs, respectively) of representative results. In the regions with catalyst, the SWNTs (diameters in the range between 0.5 and 3 nm) adopt a nearly random network geometry, consistent with our previous results with uniformly deposited catalyst at comparable coverages (Supporting Information). The low degree of alignment in this case is likely due to adverse effects of unreacted catalyst particles ($\sim 90\%$ of the catalyst does not react to form SWNTs) that coat the growth surface. In the absence of these particles, the SWNTs prefer to grow in an aligned geometry. The results of growth with patterned catalyst, as illustrated in Figure 2, are consistent with this expectation. In particular, nearly perfectly aligned, high-coverage arrays of SWNTs emerge, at angles along the preferred growth direction, from the edges of random networks in the patterned regions. Figure 2a provides an SEM image of an edge (dashed line) between a region of the substrate with (top) and without (bottom) catalyst. This effect can be exploited to obtain large-area, high-coverage aligned arrays of tubes by use of stripes of high-coverage regions of ferritin patterned with orientations perpendicular to the SWNT growth direction. Figure 2b–d illustrates the results of this approach. These levels of coverage (~ 4 SWNT/ μm) and alignment (99% of the SWNTs between the catalyst

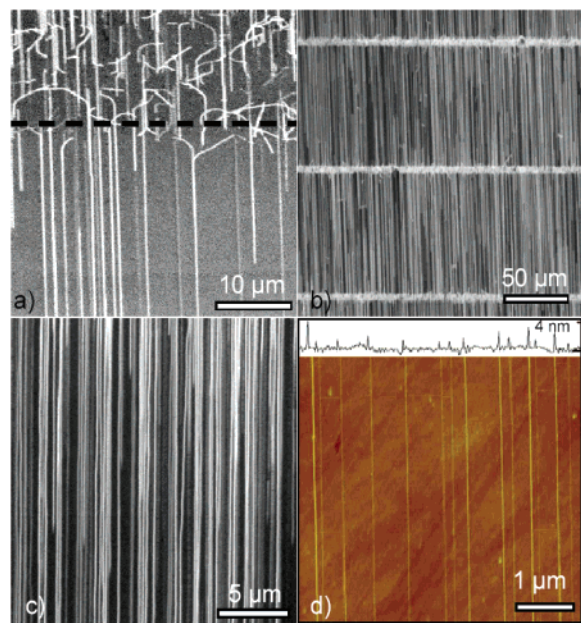


Figure 2. Images of SWNTs grown using patterned ferritin catalysts on ST-cut quartz substrates. (a) SEM collected near an edge (dashed black line) between a region with (top) and without (bottom) catalyst. (b) Nearly perfectly aligned arrays of SWNT with high coverage formed using patterned stripes of catalyst oriented perpendicular to the preferred growth direction. (c) SEM and (d) AFM images of aligned tubes from this same substrate.

stripes lie within $\sim 1^\circ$ of the preferred growth direction) significantly exceeded those that we were able to obtain with unpatterned catalyst.

Patterned catalyst on quartz substrates also enables formation, in a single step, of high-coverage random networks of SWNTs self-aligned with, and electrically interfaced to, the arrays. Such arrangements of SWNTs are important for classes of transistors and other devices that use networks and arrays for the conducting and semiconducting elements, respectively. Figure 3 presents SEMs that illustrate this type of growth capability, in which aligned SWNTs bridge the gap between large pads of random networks. Relatively few SWNTs emerge from edges of the pads that lie along the direction of preferred growth (Figure 3d), consistent with a strong driving force for alignment. Even more geometrically elaborate structures of aligned and network SWNTs are possible (Supporting Information).

To demonstrate the possibility of using such arrangements of SWNTs for transistors, we deposited a $1\text{-}\mu\text{m}$ -thick layer of a photodefinable benzocyclobutene (BCB, Dow Chemical) on top of SWNTs in geometries similar to those in Figure 3 to form a gate dielectric, followed by $2/50\text{ nm}$ of Ti/Au to form a gate electrode. The resulting devices behave like transistors in which the networks form the source/drain electrodes and the arrays form the channel, when the gate electrode overlaps only the channel region. Figure 3e shows transfer characteristics for devices with channel lengths and widths of 100 and $200\text{ }\mu\text{m}$, respectively; the gates in these cases overlap both the channel and parts of the network electrodes ($V_d = 5\text{ V}$). Because metallic SWNTs are present, the ratios of on and off currents are less than 10 (black curve in Figure 3e). A high on/off ratio of ~ 1000 can be obtained using low-density SWNT electrode (red curve in Figure 3e and curves in Figure 3f), although in this case gate modulation of the network-based electrodes contributes to the response. Selective removal of metallic tubes in the channel, by procedures such as electrical burnout or chemical functionalization, can be used to improve these types of devices.

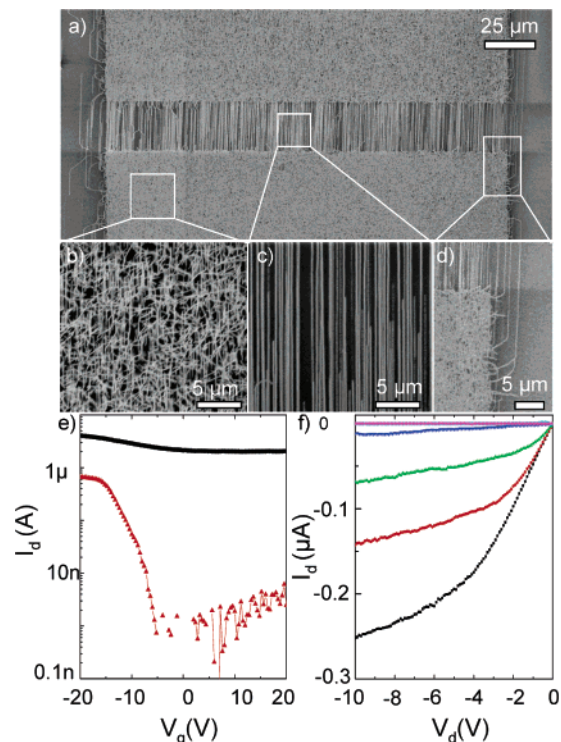


Figure 3. SEM images of SWNT grown using catalyst particles patterned in two square regions to form an arrangement of SWNTs suitable for use in a thin-film-type transistor. (a) SWNT network “electrodes” connected by a “channel” of aligned SWNTs. (b) Electrode and (c) channel regions. (d) Corner of an electrode illustrating the preferential growth. (e) Transfer and (f) output characteristics of transistors that use random networks of SWNTs as the source and drain electrodes and aligned arrays of SWNTs as the semiconducting channel. $V_g = -20$ to 0 V from the bottom.

In summary, this paper introduces new capabilities for creating arrangements of SWNTs that could be useful for applications in thin-film electronics. These techniques complement other reported approaches and may facilitate the use of SWNTs in practical devices.

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Supporting Information Available: SEM images of different density SWNT grown with patterned and unpatterned catalyst and geometrically elaborate structures of aligned and network SWNT. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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