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Aligned Arrays of Single-Walled Carbon Nanotubes Generated from Random Networks by Orientationally Selective Laser Ablation

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ABSTRACT

This paper presents results on the selective ablation of individual single-walled carbon nanotubes by use of intense picosecond laser pulses. Linearly polarized pulses ablate only those tubes that are oriented substantially along the polarization direction. When applied to random submonolayer networks of tubes on solid supports, this procedure can produce collections of aligned tubes oriented perpendicular to the polarization direction. Detailed examples highlight essential aspects of the approach and some features of the underlying physics that governs the process. Thin film transistors that use networks of tubes that have been laser processed in this manner show extremely high orientational anisotropy in the effective mobility. The results could be important for transistors that have potential applications as sensors or logic elements in macroelectronic systems or for optical elements with highly anisotropic properties.

The remarkable characteristics of single-walled carbon nanotubes (SWNT) make them interesting electronic materials for applications in electrical and optical sensors, nanoelectronic devices, and in new classes of systems that involve large area flexible circuits, also known as macroelectronics. In the latter class of device, parallel arrays or random networks of tubes act as effective semiconductor layers for high performance thin film type transistors.[1−5] In many cases, these devices can benefit from collections of tubes that have narrow distributions of orientations. Past work shows that certain solution deposition techniques can yield aligned tubes.[6−9] Directed growth methods can also produce some preferred orientation.[10−14] This paper provides an approach that separates completely the steps of growth and deposition from those of alignment. It involves exposing unaligned random networks of SWNTs to high intensity, linearly polarized laser pulses to ablate selectively tubes that lie along the polarization direction. In this manner, the laser ablation creates, from an orientationally disordered collection of SWNTs, well aligned tubes oriented in a direction that is perpendicular to the polarization. The paper begins by describing the setup and the laser sources. A variety of ablation results provides insights into the capabilities of the method and the underlying physics. Thin film transistors made using collections of SWNTs exposed to linearly polarized light show behavior that depends strongly on the orientation of the channel with respect to the polarization direction. This type of process might be useful for generating well-controlled arrays of SWNTs suitable for applications in optics,[15] sensors,[16] and electronics.[5]

Figure 1 illustrates the experimental setup. The light source is an optical parametric oscillator (Euroscan picosecond OPO) that produces trains of pulses with 3 μm wavelength. Other wavelengths are possible; we also demonstrated ablation, for example, at 1064 nm and at 532 nm. The duration of the pulses is 10 ps. They are each separated in time by 10 ns and they occur in 1 μs long bursts at a repetition rate of 25 Hz. The energy per pulse is ~24 μJ, which corresponds to an average power of 60 mW. A CaF lens with 75 mm focal length focuses the laser to a spot with a diameter of 100 μm on the sample. The sample itself consists of a collection of SWNTs grown on a quartz substrate by chemical vapor deposition (CVD). Quartz was chosen to avoid absorption of the laser light by the substrate. For the CVD growth, we used ferritin catalyst (Aldrich) diluted by deionized water at a volumetric ratio of 1:200

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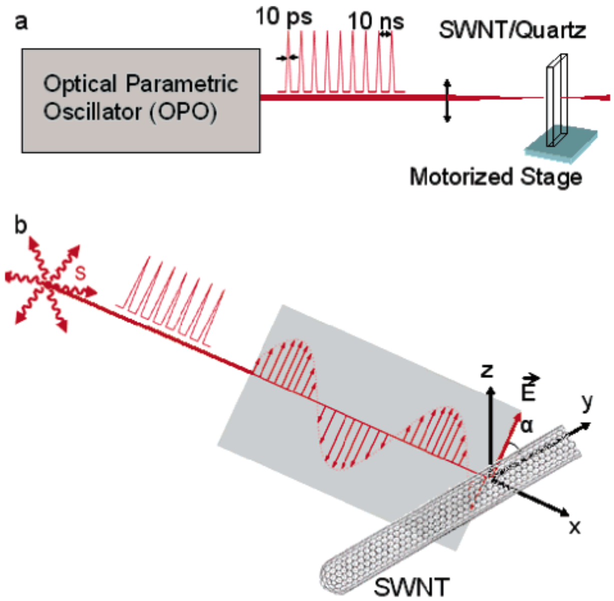

Figure 1. (a) Experimental setup and schematic illustration of direction selective laser ablation of single-walled carbon nanotubes (SWNTs). (b) Illustration of linearly polarized light (E gives the polarization direction) oriented at an angle, α, a relative to the long axis of a SWNT.

cast onto the quartz wafer. Immediately placing this substrate into a quartz tube furnace at 900 °C for 2 min followed by purging with hydrogen gas at 900 °C for 1 min and then flowing methane (500 standard cubic centimeters per minute (sccm)) and hydrogen (75 sccm) at 900 °C for 10 min grows the SWNTs. The density of tubes for the experiments described here is between 2 and 5 per square micron, with diameters between 1 and 5 nm and lengths in the range of 5−10 μm. SWNTs grown in this manner appear on the substrate with the entire range of possible orientations. A motorized sample mount provides a means to scan the laser spot over the surface of the sample in a controlled manner.

Figure 1b shows a schematic illustration of linearly polarized light incident on a SWNT. The symbol E represents the polarization direction. Since SWNTs have deeply sub-wavelength and highly anisotropic dimensions, their interaction with light strongly depends on the orientation of electric field with respect to their orientation. In particular, optical absorption is much stronger for light polarized along the tube axis than it is for light polarized perpendicular to this axis. Recent work describes models for the physics behind this anisotropy.[17−20] One can qualitatively understand the effect by analogy to absorption anisotropy in metal wires that have subwavelength widths. As a result, the total absorption is proportional to the square of the projection of the electric field onto the long axis of the tube. For laser pulses with sufficiently high intensity and short pulse duration, it is possible for this absorbed light to destroy the tubes through an ablation process. The strong dependence of the absorption cross section on orientation induces a similar dependence in the threshold for ablation. We exploit this effect to generate aligned tubes from random networks.

Figure 2 shows AFM images of SWNTs exposed to laser pulses with different intensities above ablation threshold, with fixed exposure time of 100 ms. The ablated tubes appear in these AFMs as discontinuous lines or dots that lie along the positions of tubes that existed before laser exposure. (Dots present even at low intensities are due to ferritin catalyst

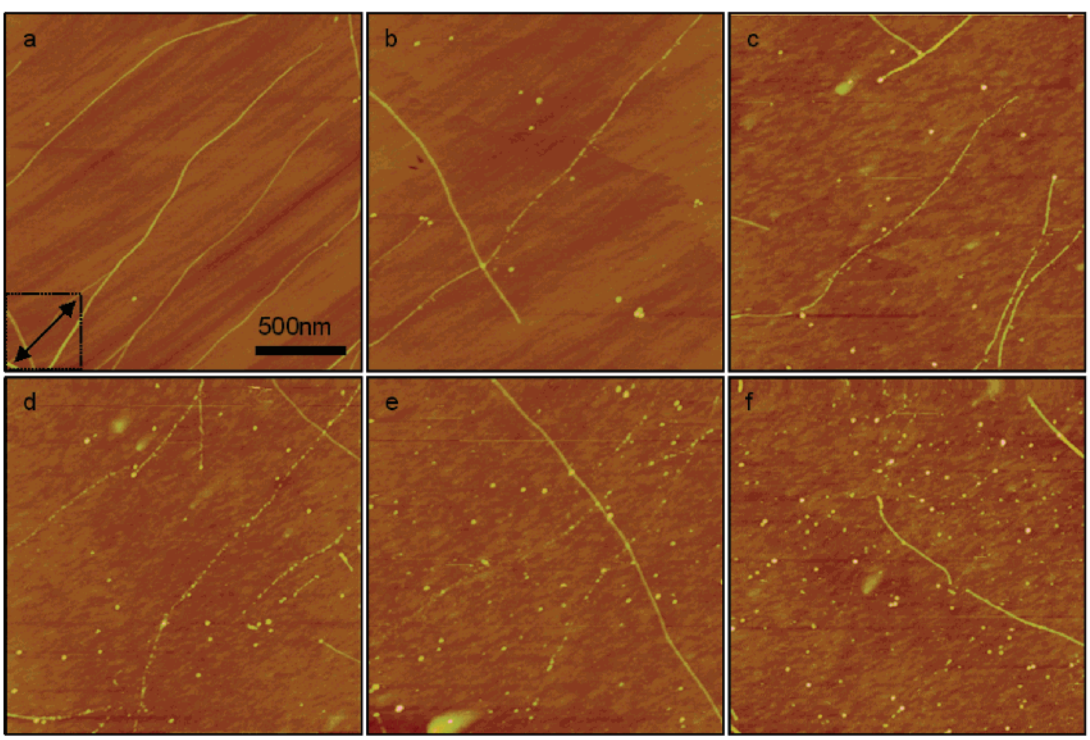

Figure 2. Series of AFM images of SWNTs exposed to laser pulses with different peak powers: (a) unexposed, (b) 13 MW/mm^2, (c) 27 MW/mm^2, (d) 40 MW/mm^2, (e) 53 MW/mm^2, and (f) 80 MW/mm^2. These data indicate that the threshold for ablation, as determined by morphological changes observable by AFM, is roughly 13 MW/mm^2.

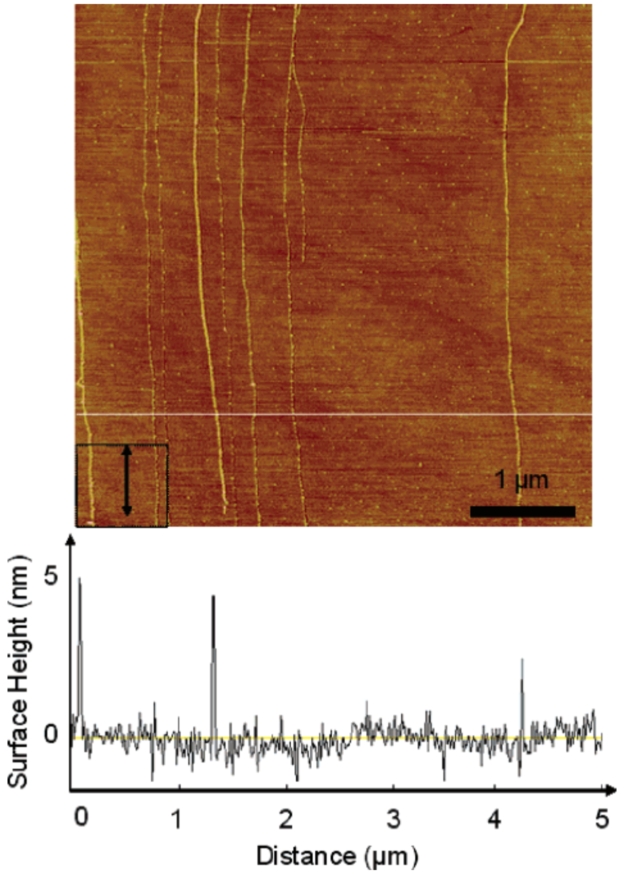

Figure 3. AFM image (top) and line scan (bottom) of an array of parallel SWNTs that have different diameters, between 1 and 5 nm. Inset shows the polarization direction of the laser. These data indicate that the laser can ablate tubes with a range of diameters. The ablation thresholds are comparable for the range of diameters studied.

particles.) This structural deformation is different for different exposure intensities. At low intensities, the tubes become discontinuous with small breaks (as observed by AFM) that appear along the lengths of the tubes. As the power increases the structural deformation becomes more pronounced and these breaks evolve into isolated dots. Figure 3 shows results from ablation of an array of parallel SWNTs that have diameters between 1 and 5 nm. Even with the laser power tuned near the ablation threshold, we did not observe a significant dependence of the ablation on the diameter or on the electronic properties (i.e., semiconducting or metallic). Similarly aligned tubes tended to ablate in a nonspecific manner at comparable thresholds. The morphologies of the ablated tubes have some similarities to those of SWNTs that are heated above 350 °C in air. Although these similarities do not provide sufficient information to draw firm conclusions on the details of the ablation process, they are consistent with ablation that has some thermal origins. Extrapolations from recent work suggest that the temperature rise in the tubes in our experiments could easily exceed 500 °C. The time constant for diffusion of heat from the tubes to the underlying substrate is on the order of ~40 ps.[21] It is therefore likely that cumulative heating from successive pulses in the train (pulse to pulse separation of 10 ns) is insignificant and that ablation can occur in a single pulse.

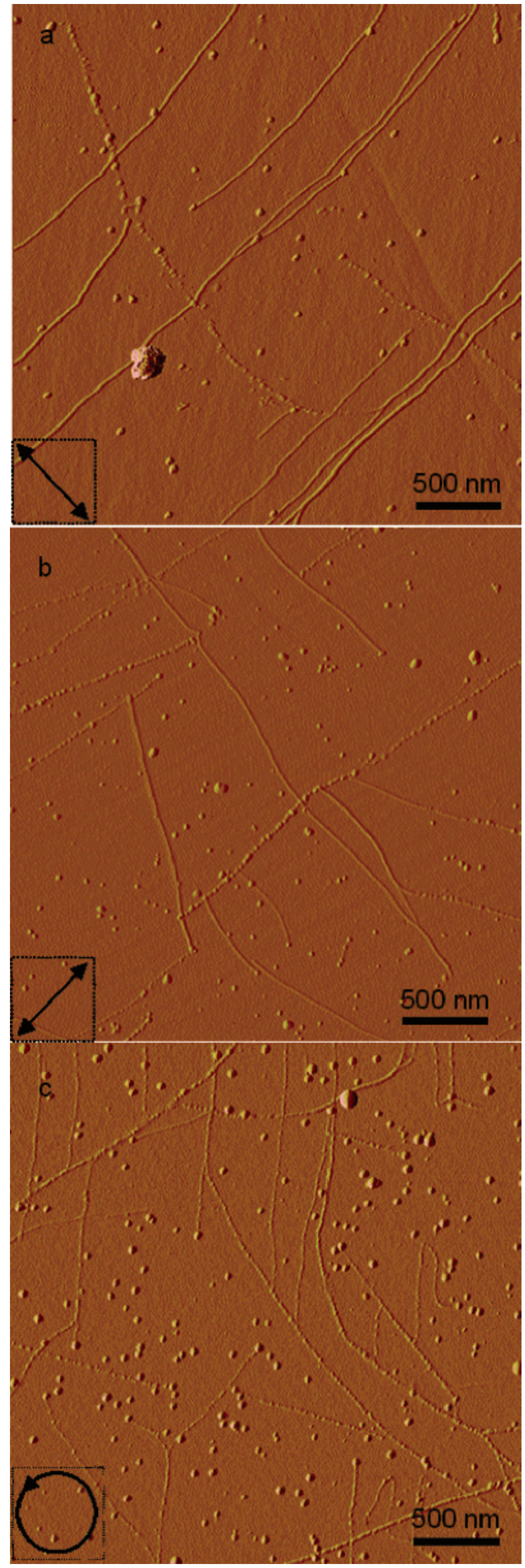

Figure 4. AFM images of SWNTs after exposure to intense laser pulses with linear polarization. The double headed arrows in the lower right portions of these images illustrate the polarization direction. The laser ablates only those tubes that are oriented substantially parallel to the polarization direction.

The makeup of the material that remains after ablation is unknown, but it likely consists, at least in part, of amorphous carbon. Additional experiments are required to understand fully these and other aspects. This paper focuses, instead,

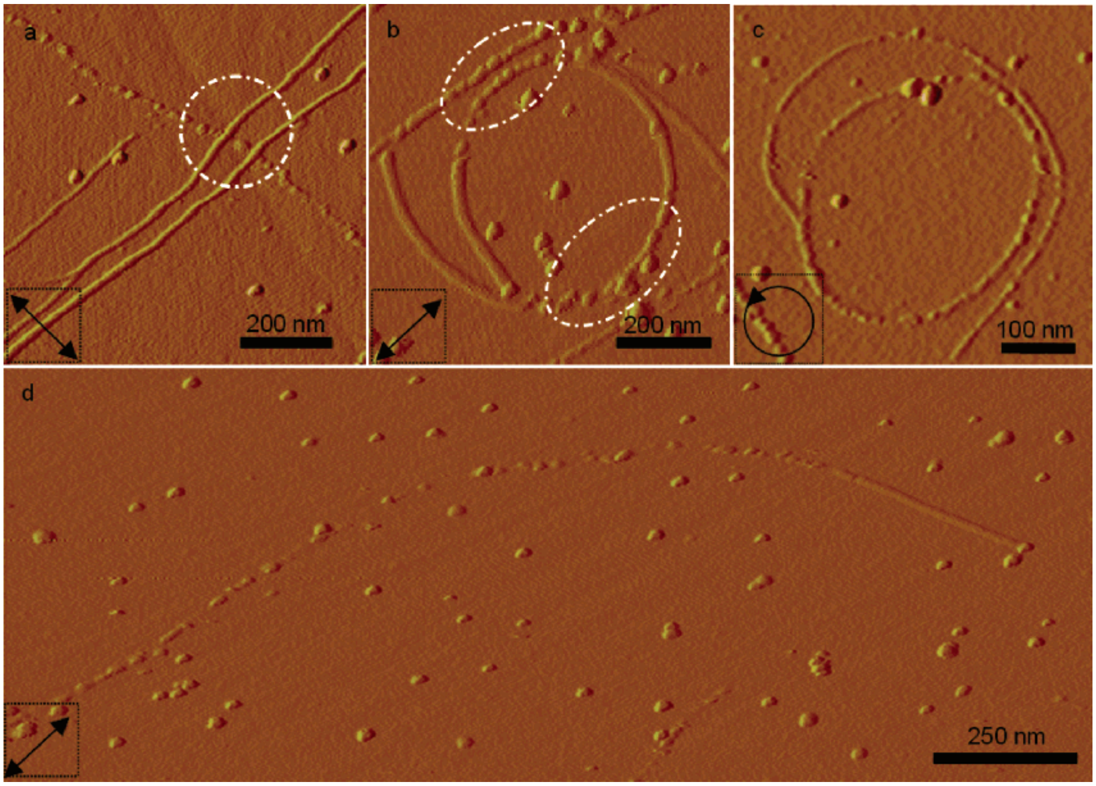

Figure 5. AFM images of different effects of laser ablation on collections of SWNTs. (a) Image that highlights the ability to ablate a SWNT without substantially affecting orthogonally aligned SWNTs that overlap with it. (b) Image of the results of ablating a semicircular SWNT with linearly polarized light; only the sides that are parallel to the polarization direction are ablated. (c) Image of a similar semicircular SWNT ablated with circular polarized light; in this case the entire length of the SWNT is ablated. (d) Image of a long curved SWNT in which only the segment that lies along the direction of linear polarization is ablated. In all frames the schematic illustrations in the lower left indicate the state of polarization; dotted white circles highlight the important parts of the images. These results provide important insights into the ablation process and the apparently small role that thermal diffusion plays in it.

on some operational features of the process and means to use it to generate aligned tube arrays for transistor applications.

Figure 4a and b shows results obtained with orthogonal linear polarizations; Figure 4c shows the case for circularly polarized light (10 μJ pulses with 300 ps duration and repetition rate of 10 kHz at 1064 nm, focused to a spot with 10 μm diameter). The insets at the bottom left illustrate the polarization states. The first two frames illustrate clearly that only tubes aligned along the polarization direction are ablated by the laser. The circularly polarized light destroys all tubes, independent of orientation, as expected due to the lack of dependence of the absorption on orientation in this case. By controlling the polarization of the laser we can select the ablation direction to generate tube arrays with well-defined orientation.

Additional aspects of the ablation process can be understood from careful examination of the effects on individual or small numbers of SWNTs. Figure 5 presents AFM images of a representative set of results. Figure 5a shows the intersection of an ablated tube with two orthogonally aligned tubes that remain unablated. To within the resolution of the AFM, the orthogonal tubes survive without any significant structural deformation due to the ablation of the tube that previously directly crossed them (on top or beneath). Theoretical studies suggest that such crossing tubes interact only with weak dispersion forces and that the contact areas at the crossing regions are small. As a result, the resistance to heat flow from one tube to another is expected to be large.[22] The results of Figure 5a are qualitatively consistent with that conclusion. Figure 5b shows an AFM image of a ring-shaped SWNT ablated with linearly polarized pulses. The parts of this ring that have tangents parallel to the polarization direction are ablated, while the other parts remain unaffected. The results show that individual nanotubes can be structured by laser ablation. This observation is somewhat surprising if the ablation process is fundamentally thermal, since SWNTs are known to have extremely high thermal conductivities. It might be understood, however, based on the combined effects of efficient heat flow to the substrate and a sharp threshold for thermal ablation. If we assume that the time for flow of heat to the substrate has a characteristic time scale of 40 ps, then the diffusion length is $\sim$200 nm if we assume that the diffusivity of the tubes is $\sim$10 cm^2/s. Figure 5c shows another AFM image of a ring-shaped SWNT exposed to circularly polarized laser pulses. Here, the entire ring is ablated, as expected based on the lack of dependence of absorption with orientation, in this case. An image of a long curved SWNT after ablation appears in Figure 5d. Ablation ceases, apparently abruptly, beyond a certain angular mismatch between the tube axis and the polarization direction. Taken together, these AFM images illustrate the

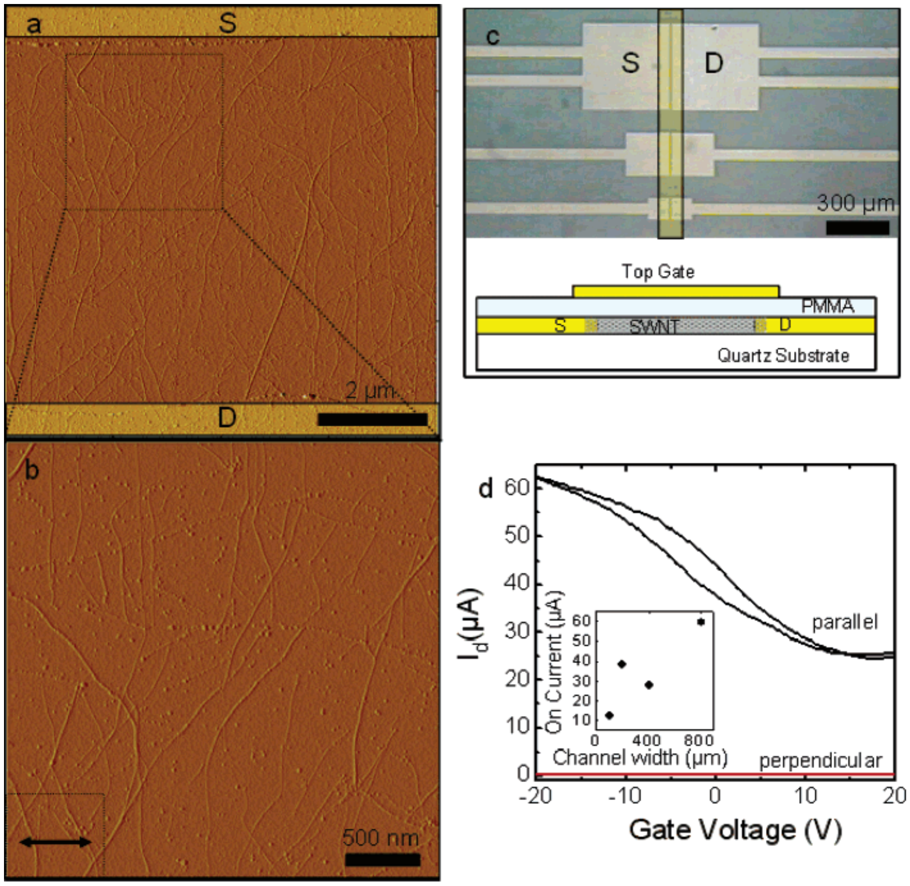

Figure 6. Field effect transistor that uses a collection SWNTs, some of which have been destroyed by laser ablation. (a) AFM image of the channel of a typical device; the source and drain electrodes are at the top and the bottom. The distance between them is 6 μm. (b) Magnified view of part of the channel region of the device. The inset in the bottom left illustrates the direction of linear polarization of the light used to selectively ablate some of the tubes. (c) Optical image of an array of devices (top) and schematic illustration of the device geometry (bottom). These transistors use a 1 μm thick layer of PMMA deposited onto the tubes as a gate dielectric. (d) Current/voltage response of devices that have channels oriented parallel (black) and perpendicular (red) to the polarization direction of the linearly polarized laser pulses used for ablation. These data show clearly that the laser destroys SWNTs that lie along the polarization direction.

high precision in control of SWNT shapes and orientations that is possible with laser ablation.

As an application example, we used this technique to fabricate thin film transistors that incorporate an aligned collection of SWNTs as an effective semiconductor layer, by starting with an orientationally disordered network. Figure 6a shows an AFM image of channel region of a completed device with 6 μm channel length. The source and drain are illustrated as colorized regions at the top and bottom of this image. The film of SWNTs was grown on a quartz substrate in the manner previously described and then exposed with linearly polarized laser pulses to destroy tubes along the polarization direction. Figure 6b shows a magnified AFM image of the channel region. Directionally ablated tubes can be seen clearly. Source/drain contacts of Ti/Au (3 and 25 nm thicknesses) were fabricated on the exposed film by liftoff with a poly(methyl methacrylate) (PMMA) resist patterned by deep ultraviolet photolithography. A 1 μm thick PMMA layer spin cast on top of this structure formed a dielectric for the Au gate electrode that was deposited through a shadow mask. Figure 6c shows an optical micrograph of an array of devices (top) and a schematic illustration of the device geometry (bottom). Figure 6d presents the transfer characteristics of typical devices that have their channels aligned parallel and perpendicular to the direction of the aligned tubes. The results clearly show the expected anisotropic response. The currents in the perpendicular device are about 1 μA or less; the gate leakage is less than a few nA in both cases. The inset in Figure 6d shows the scaling of the on current in the case of a series of devices with the parallel orientation. The current depends linearly on the channel width, as expected for devices that use uniform thin films of semiconductors and that are decoupled well from one another. (This latter feature is due at least partly to poor conductivity through the film in the perpendicular direction.) The observation of large currents in the parallel devices is consistent not only with orientationally selective burning, but it also reveals additional information concerning ablation at tube/tube crossings (e.g., Figure 5a). For the SWNT arrays used in these devices, nearly all of the unablated tubes have at least one crossing point with an ablated tube. If the ablation destroyed both tubes at this crossing point, then the electrical continuity of the unablated tube would be degraded or eliminated. Our electrical measurements are consistent only with relatively minor (from an electrical standpoint) or no degradation.

In summary, this paper introduces a convenient way to control the alignment of SWNT networks through laser ablation. Thin film transistors built with such laser processed tubes show good performance and the expected orientational anisotropy. This tool may be valuable for a range of device applications. The basic mechanisms of the ablation and the nature of the products of this process represent topics for future research.

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Supporting Information Available: AFM images of a laser ablated SWNT and a SWNT after thermal treatment. This material is available free of charge via the Internet at http://pubs.acs.org.

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